Preparation of a Conjugated Molecule and Materials for use therein

The present invention relates to a method for preparing a conjugated molecule such as a conjugated polymer or oligomer (in particular a polyaryl, polyheterocycle (*e.g.* polyheteroaryl) or oligoheterocycle including a block oligoheterocycle) comprising an improved coupling step.

Electroactive materials such as polyheteroaryls and oligoheteroaryls are gaining widespread academic and commercial interest due to their optical and electronic properties which may allow exploitation in electronic devices such as transistors (*e.g.* field effect transistors FETs useable in mobile phones, calculators, smart cards, etc) and LED's. For example, organic semiconductors have the potential advantage over inorganic semiconductors of low cost fabrication and patterning, large area fabrication and greater scope for tuning. Alternatively, synthesis from acyclic precursors can lead to high purity compounds but can be highly convoluted and significant material losses must be tolerated.

Successful organic semiconductors are likely to have a significant degree of control in regioregularity so as to allow efficient alignment and ordering in the solid state. As electrical performance of such materials improve, their manufacture is set to become one of the major speciality chemical opportunities of this century.

Although solution phase chemistry may be used to target polyheterocycles and oligoheterocycles using repetitive coupling reactions, the purification strategies required to meet the requisite levels of purity are inefficient rendering the methods of questionable commercial applicability. Moreover conventional methods for preparing oligoheterocycles (such as oligothiophenes) using solution phase cross-coupling (*e.g.* Suzuki, Kharasch, Stille or Negishi type processes) are plagued by undesirable side reactions such as homocoupling and loss of functional groups making purification arduous and inefficient.

It is desirable therefore to provide a process which allows control over the number of monomer units incorporated into the oligomer chains and/or the sequence of monomer units if more than one type of monomer unit is present.

The advantages of solid phase chemistry, i.e. chemistry using solid supports, over solution phase chemistry include ease of purification, amenability to automation, the ability to use excess reagents to drive reactions to completion without the penalty of making purification tedious and dilution effects (site isolation) which prevent homocoupling. For these reasons, solid phase synthesis is seen as an attractive alternative for preparing polyheterocycles and oligoheterocycles on a large scale but as yet has undergone little investigation. Synthesis on a solid polymer support necessitates two additional steps to solution phase synthesis, namely covalent attachment of the first monomer to the support via a linker and cleavage of the polymer from the support.

It is desirable that on cleavage the linker group be eliminated from the conjugated molecule and optionally replaced by a functional group for use in a further reaction.

One drawback of the application of solid phase synthesis is that on cleavage from the resin/linker an undesirable functional group may be left on the molecule that may be deleterious to the performance of the polymer material. Attachment in known processes is typically via "protecting group" based linkers meaning that a functional group (e.g. OH, COOH) incorporated in the first monomer is regenerated on polymer cleavage. Such functionality may be undesirable for the envisaged applications. For example, Malenfant and Frèchet, Chem. Commun, 1998, 2657-2658 disclose the synthesis of asymmetric oligothiophenes bound by an ester linkage to a chlormethylated macroporous resin using alternating bromination and Stille coupling reactions. Malenfant utilizes a Wang resin (**1** in Figure 1) which leaves an ester that requires subsequent decarboxylation. A similar resin supported preparation of benzyl ester capped polythiophenes is disclosed in Kirchbaum et al, Synthetic Metals, 119 (2001), 127-128 using alternating Suzuki/iodination coupling steps. Bäuerle et al, J. Org. Chem., 2000, 65, 352-359 avoided this complication using a silicon-based linker (**2** in Figure 1) that allowed traceless cleavage via *ipso*-protodesilylation, i.e. replacement of silyl group by a proton.

Thus viewed from one aspect the present invention provides a method for preparing a conjugated molecule comprising a first monomer coupled to a second monomer, said method comprising:

(A) linking the first monomer to a solid support via the germanium atom of a germyl linking group;

(B) if necessary activating a position on the first monomer and coupling the first monomer to a second monomer in a coupling position to form a bound conjugated molecule, wherein the second monomer has a protecting group in a non-coupling position if necessary repeating this coupling to obtain a higher degree of conversion;

(C) optionally removing the protecting group and repeating (B) with one or more further monomer molecules one or more times, optionally using monomer molecules without protecting groups or removing protecting groups as required if present

(D) if desired removing the protecting group; and

(E) *ipso*-degermylation to release the bound conjugated molecule.

By *ipso*-degermylation is meant replacing the germyl group by a proton or other group which may be a functional group permitting further reaction.

The product may be a homopolymer or copolymer.

Preferably the solid phase synthesis of the conjugated molecules such as polyaryls or polyheterocycles is improved by using a "double coupling strategy" which permits multiple coupling reactions for a single coupling step such that the level of coupling may be driven to high levels to increase purity of the final product. The present invention also provides a solid phase synthesis of conjugated molecules in which a first monomer linked to a solid support by a germyl linking group is coupled to a protected

second monomer whose protecting group renders the coupled product inert to subsequent coupling.

Thus, in such solid phase chemistry a solid support which comprises bound germyl linking groups is coupled with the first monomer optionally in at least two successive stages to maximise the proportion of the germyl groups so coupled with the first monomer and coupling of each monomer (or subsequent oligomer) linked to the support to subsequent protected monomers may be carried out in at least two successive stages to maximise the proportion of the linked monomer or oligomer which is reacted. Should a coupling group be lost before completion of the reaction with the second or subsequent monomer it is preferable, if possible, to reform the group and to react again with the said monomer until the desired product is obtained. By these means the uniformity of the product is maximised.

The term conjugated molecule is intended to cover high or low molecular weight polymers and co-polymers including oligomers and co-oligomers. Preferably the conjugated molecule is a conjugated oligomer. Typically the method may be used to synthesise a range of conjugated molecules from simple dimers to more complex block co-polymers (such as block co-oligomers).

The term monomer is intended to cover single monomer units or a block of monomer units.

In an embodiment of the invention, each of the first, second and n^{th} monomers are capable of contributing to the -system of the conjugated molecule. For example, the first, second and n^{th} monomer may be independently selected from the group of monomer units consisting of an unsaturated monocyclic or polycyclic (*e.g.* fused polycyclic) hydrocarbon (*e.g.* a carboaromatic) monomer unit which is optionally ring substituted, an unsaturated monocyclic or polycyclic (*e.g.* a fused polycyclic) heterocyclic (*e.g.* heteroaromatic) monomer unit which is optionally ring substituted, an unsaturated acyclic hydrocarbon bridging monomer unit and a heteroatomic (or polyheteroatomic) bridging monomer unit. The first, second and n^{th} monomer may be the same or different. Optional ring substituents may be chosen to enhance the electronic (or other) properties of the conjugated molecule (*e.g.* a substituent which has an electron withdrawing or donating effect).

Preferably the conjugated polymer is a polyheterocycle, wherein at least one of the first, second and n^{th} monomers (preferably at least the first monomer) is an optionally ring substituted heterocyclic monomer unit. Preferably more than one of (*e.g.* all of) the first, second and n^{th} monomers is an optionally ring substituted heterocyclic monomer unit. Preferably at least one of the first, second and n^{th} monomers is a 5- or 6-membered optionally ring substituted heterocyclic monomer unit. The optionally ring substituted heterocyclic monomer unit may contain one, two or three heterocyclic atoms which may be the same or different. Preferably the (or each) heterocyclic atom is selected from the group consisting of nitrogen, sulphur, oxygen, phosphorous and selenium, preferably the

group consisting of nitrogen, oxygen and sulphur, particularly preferably the group consisting of nitrogen and sulphur.

The term polyheterocycle is intended to cover high or low molecular weight polymers and co-polymers including oligomers and co-oligomers. Preferably the polyheterocycle is an oligoheterocycle. Typically the method may be used to synthesise a range of polyheterocycles from simple dimers to more complex block co-polymers (including block co-oligomers).

Preferably at least one of the first, second and n^{th} monomers (preferably at least the first monomer) is an optionally ring substituted unsaturated monocyclic or polycyclic (e.g. fused polycyclic) hydrocarbon (e.g. a carboaromatic) monomer unit. For example, the conjugated molecule may be a polyaryl. Particularly preferably at least one of the first, second and n^{th} monomers is an optionally ring substituted phenylene, styryl or anilino monomer unit suitably of formula $-Ar'NAr''Ar'''-$ is present, the groups Ar', Ar'' and Ar''' being aryl groups, in which the aryl groups may be phenyl groups. Ar''' may be substituted (e.g. o- or p-substituted) with a group which has an electron withdrawing or donating effect.

Preferably at least one of the first, second and n^{th} monomers is an unsaturated acyclic hydrocarbon bridging monomer unit selected from the group consisting of alkeno and alkyno bridging monomer units. Preferably the unsaturated acyclic hydrocarbon bridging monomer unit is of formula $[CR=CR]_n$ (where n is 1 to 5, preferably 1 to 3 and R is hydrogen or a C_{1-6}-alkyl group) or $[C\equiv C]_m$ (where m is 1 to 3). Preferred examples are etheno, ethyno and buta[1,3]dieno bridging monomer units.

By way of example, at least one of the first, second and n^{th} monomers, i.e. any of the monomers, is selected from the group of monomer units consisting of optionally ring substituted thiophene, furan, pyridine, imidazole, isothiazole, isooxazole, pyran, pyrazine, pyridazine, pyrazole, pyridine, pyrimidine, triazole, oxadiazole, pyrrole, indazole, indole, indolizine, pyrrolizine, quinazoline, quinoline and phenyl. Preferably at least one of (preferably more than one of) the first, second and n^{th} monomer units is selected from the group consisting of optionally ring substituted thiophene and pyridine and particularly preferably is thiophene which may be substituted at the 3- or 4-position with an alkyl group (*e.g.* a C_{1-12}-alkyl such as a hexyl or octyl) or an aryl (*e.g.* a phenyl) group.

If desired at least one of the first, second and n^{th} monomers (preferably the first and second monomer) may be a block of monomer units, each monomer unit being as hereinbefore defined.

The conjugated molecule typically comprises up to 20, preferably up to 10 monomer units.

Two directional synthesis may be possible if the first monomer has two reactive positions. For example, where the first monomer is thiophene linked to germanium at the 3-position, it may be possible to simultaneously couple at positions 2- and 5- without separate synthetic steps.

Although any suitable protecting group may be used to protect the non-coupling position of the second monomer, silyl based protecting groups are preferred to exploit favourable differences in reactivity between germanium and silicon. Examples include Me_3Si (TMS), Et_3Si, $^iPr_3Si$, $Me_2{}^tBuSi$, Me_2PhSi. A particularly preferred example is TMS (trimethyl silane) or tert. butyl dimethyl silane. Corresponding silyloxy groups may also be used.

Step (D) may be carried out before, after or simultaneously with step (E) leading to symmetrically end functionalised or -telechelic molecules with useful end functionality. A silyl protecting group may be removed in step (C) nucleophilically with basic sources (*e.g.* K_3PO_4 orCs_2CO_3) and/or fluoride sources (*e.g.* CsF or $^nBu_4NF$) or electrophilically (*e.g.* using electrophiles described below).

The *ipso*-degermylation of step (D) may be *ipso*-protodegermylation or electrophilic *ipso*-degermylation (*e.g. ipso*-halodegermylation).

By way of example, *ipso*-protodegermylation may be carried out using a strong organic acid (for example trifluoroacetic acid (TFA), HCO_2H, AcOH, $ClCH_2CO_2H$ or Cl_2CHCO_2H), a mineral acid (for example HCl, H_2SO_4 or HF) or a source of fluoride ions (for example CsF or Bu_4NF) with conditions generally milder than those used for removal of the protecting group for example a silyl group.

Electrophilic *ipso*-degermylation may be carried out using a source of halonium ions (F^+, Cl^+, Br^+ or I^+), NO^+, NO_2^+, SO_3^+, RCO^+, RSO_2^+, $BHal_2^+$(*e.g.* BCl_2^+) or $B(OH)_2^+$. Where conditions are mild, the protecting group may be left intact to release a protected conjugated molecule. Subsequent removal of the protecting group in step (C) using a different electrophile leads advantageously to an unsymmetrical conjugated molecule. Under more forcing conditions, the protecting group may be removed simultaneously (*e.g.* electrophilic *ipso*-desilylation) advantageously releasing a symmetrically end functionalised conjugated molecule.

ipso-halodgermylation may be carried out using a source of halonium ions (X^+). For example, *ipso*-bromodegermylation may be carried out using a source of bromonium ions (Br^+) such as bromine or N-bromosuccinimide (NBS), *ipso*-iododegermylation using a source of iodonium ions (I^+) such as iodine, ICl or N-iodosuccinimide (NIS) and *ipso*-chlorodegermylation using a source of chloronium ions (Cl^+) such as N-chlorosuccinimide (NCS), dichloramine-T or chlorine. In the case of polymers and oligomers which are not adversely affected by oxidising conditions an advantageously cheap and therefore preferred step for preparing halonium ions is to use a group I metal halide together with an oxidant. For example, NaBr may be used with an oxidant such as H_2O_2 or (preferably) dichloramine-T to produce bromonium ions.

In a preferred embodiment, step (E) comprises:

ipso-degermylation using a functionalised block conjugated polymer AY.

This embodiment advantageously releases block co-oligomers with varying (but precisely defined) topology. Preferably compound AY is a functionalised block conjugated polymer (or a functionalised block conjugated oligomer) wherein the block conjugated polymeric group Y is preferably a block of monomeric units as hereinbefore defined. For example, group Y may be a dimeric, trimeric, tetrameric, pentameric or hexameric thiophene or pyridine block. Functionality A is typically bromine or iodine preferably bromine.

New C-C bonds may be advantageously formed by *ipso*-degermylative cleavage to leave an end capping group which may be tailored to introduce desirable electronic properties to the conjugated molecule. For example, *ipso*-degermylation may be carried out using a source of acylium ions such as a Freidel-Crafts reagent (*e.g.* carboxylic acid chloride and Lewis acid) to leave a ketone end group. For example, *ipso*-degermylation may be carried out using germyl-Stille type cleavage with an aryl, heteroaryl, vinyl, benzyl, allyl, alkynyl or propargyl halide (I, Br or Cl), sulphonate ester (triflate, nosylate, mesylate or tosylate) or diazonium salt (N_2^+) in the presence of a catalytic amount of Pd(0) having suitable ligands (*e.g.* phosphine ligands) and a reagent capable of rendering germanium hypervalent (*e.g.* a source of fluoride ions such as CsF or Bu_4NF) to leave an aryl, heteroaryl, vinyl, benzyl, allyl, alkynyl or propargyl end group respectively. Generally *ipso*-degermylative cleavage may be carried under conditions suitable to leave the protecting group intact. This may be followed by electrophilic removal of the protecting group (step (D)) with an electrophilic group as described above or nucleophilic removal of the protecting group with a base (*e.g.* CsF or K_3PO_4) to give unsymmetrical conjugated molecules.

Electrophilic *ipso*-degermylation advantageously leaves end functionality on the conjugated molecule which subsequently may be displaced by groups chosen to enhance the properties (*e.g.* electroactive properties) of the conjugated molecule. For example, the end functionality may be tailored to facilitate solution phase synthesis of block co-oligoheterocycles thereby giving greater versatility in preparing potentially useful electroactive materials.

Thus in a preferred embodiment, step (E) comprises:

(E1) *ipso*-degermylation using an electrophilic group E to release the bound conjugated molecule (P) having end functionality E;

and the method further comprises:

(E) reacting the conjugated molecule (P) having end functionality E with a compound A'Y' wherein group Y' is capable of displacing end functionality E.

Preferably end functionality E is other than an end carboxyl (or a derivative (*e.g.* ester)) thereof. Particularly preferably the end functionality E is bromine, iodine or a boronic group such as boronic acid groups or derivatives thereof (*e.g.* ester derivatives thereof). Preferred are boronic acid groups of formula $-B(OR)_n$ (as defined hereinafter), particularly preferably $B(OH)_2$.

Group Y' may be an end capping group such as a linear or branched alkyl (*e.g.* C_{1-6}-alkyl), aryl, benzyl, vinyl, propargyl, allyl or alkynyl group or a conjugated molecule such as an oligoheterocyclic group.

Preferably compound A'Y' is a functionalised block conjugated polymer (or a functionalised block conjugated oligomer) wherein the block conjugated polymeric group Y' is preferably a block of a conjugated molecule as hereinbefore defined. For example, group Y' may be a dimeric, trimeric, tetrameric, pentameric or hexameric thiophene or pyridine block. Functionality A' is typically bromine, iodine or a metallic for example a organometallic functionality such as an organoboron, organomagnesium, organozinc or organotin functionality. Preferred is a boronic functionality (*e.g.* an organoboron functionality $-B(OR)_n$ as defined hereinafter), particularly preferably $B(OH)_2$. In this embodiment, step (D) may be carried out in the presence of a catalyst such as palladium or nickel.

It will be appreciated that this embodiment permits the synthesis of block conjugated molecules with a variety of precisely defined topologies. For example, it would be possible to synthesise a range of block conjugated co-oligomers such as PY', PY'P, PY'P' (wherein P and Y' are as hereinbefore defined and P' which is different to P is a block of monomer units as hereinbefore defined).

The precise conditions for the *ipso*-degermylation of step (E) may be optimised by the skilled person to reflect its sensitivity to the electronic nature of the conjugated (*e.g.* heterocyclic) system. For example, electron rich heterocycles such as thiophene generally cleave most readily whereas electron deficient heterocycles such as pyridine require more forcing conditions. Moreover the conditions can be tailored to carry out step (D) before, after or simultaneous with step (E).

Step (B) may be carried out using a suitable coupling protocol. Many such protocols are established in the art and will be familiar to the skilled person (see *inter alia* Loewe *at al*, Adv. Mater.1999, 11, 250-257). These include Suzuki, Kharasch (*e.g.* McCullough), Stille and Negishi type reactions, preferably Suzuki or Kharasch type reactions. Step (B) is typically carried out in the presence of a transition metal catalyst such as nickel or (preferably) palladium.

In a preferred embodiment, step (B) further comprises:

(B1) activating for example by halogenating the first monomer in a coupling position; and

(B2) reacting the product of step (B1) with the second monomer metallated in the coupling position.

This embodiment relies on the fact that the immobilised first monomer may be selectively halogenated in the coupling position without *ipso*-degermylative cleavage.

Prior to step (B1), the method may further comprise: (B0) lithiating the first monomer for example using nBuLi or lithium disopropylamide (LDA) in the coupling position.

Step (B1) may be carried out using bromine, iodine (*e.g.* in the presence of a mercury salt such as acetate or hexanoate) or (preferably) a milder source of iodonium ions. The source of iodinium ions is preferably 1,2-diiodoethane. Particularly preferably halogenation with 1,2-diiodoethane is carried out in reduced ambient light (*e.g.* in darkness). Particularly preferably halogenation is carried out with 1,2-diiodoethane in an amount at least one fold excess of the amount of lithiating agent (preferably LDA) used in step (B0).

In an alternative embodiment, step (B) comprises:

(B1') metallating the first monomer in a coupling position; and

(B2') reacting the product of step (B1') with the second monomer halogenated in the coupling position.

The alternative embodiment relies on the fact that the immobilised first monomer may be selectively metallated (or transmetallated) in the coupling position without *ipso*-degermylative cleavage. For example, the immobilised first monomer may be transmetallated using nBuLi and an organometallic transmetallating compound.

In a preferred alternative embodiment, step (B1') comprises: (B1'a) lithiating the first monomer at the coupling position (for example in the presence of nBuLi) and (B1'b) transmetallating the first monomer at the coupling position. The first monomer is advantageously stable to strong bases such as nBuLi. For pyridine and thiophene, this generally leads to lithiation and transmetallation at the coupling position adjacent the heterocyclic atom.

The first or second monomer may be metallated (or transmetallated) at its coupling position with a metallic group e.g. an organometallic group. For example, the metallic group may be selected from organoboron, organomagnesium, organotin and organozinc groups. Preferred are organoboron groups such as boronic acid groups or derivatives thereof (*e.g.* ester derivatives thereof). Particularly preferably the organoboron group is of formula:

$$-B(OR)_n$$

(wherein: n is 2 or 3; and each R is independently hydrogen or an optionally substituted linear or branched C_{1-6}-alkyl group or two groups R represent an optionally substituted alkano bridging group between two oxygen atoms).

For the purposes of this specification we define boron as being a metal.

For example, two groups R may represent an optionally substituted ethano or propano bridging group between two oxygen atoms. Preferred is an ethano bridging group between two oxygen atoms which is preferably dialkyl (*e.g.* dimethyl) substituted at each carbon.

Preferred is a hypervalent boronate complex or a boronic ester group (or a hypervalent complex thereof). It is advantageous to use a weak base (*e.g.* $NaHCO_3$). Particularly preferred is a hypervalent boronate complex which advantageously does not require the addition of base (and therefore essentially does not remove any silyl protecting group). The hypervalent boronate complex may be a hypervalent alkyl boronate complex with a suitable metal counterion (*e.g.* Na or (preferably) Li). Preferred is the hypervalent ethyl boronate complex, particularly preferably in the absence of a base.

Certain of the hypervalent organoboron intermediates useful as first and/or second monomers in the method of the invention may lead to improved coupling and being novel are therefore patentably significant *per se*.

Viewed from a further aspect the present invention provides a compound of formula:

$$[X\text{-}B(OR)_3]M$$

wherein:

M is a counter ion;

X is an optionally ring substituted unsaturated monocyclic or polycyclic (*e.g.* a fused polycyclic) hydrocarbon or heterocyclic moiety; and

each group R is independently hydrogen or an optionally substituted linear or branched C_{1-6}-alkyl group or two groups R represent an optionally substituted alkano bridging group between two oxygen atoms.

The group $B(OR)_3$ may include a pinacolato group. For example, two groups R may represent an optionally substituted ethano or propano bridging group between two oxygen atoms. Preferred is an ethano bridging group between two oxygen atoms which is preferably dialkyl (*e.g.* dimethyl) substituted at each carbon.

In a preferred embodiment, each R is the same and is a C_{1-6}-alkyl group. The hypervalent boronate complex of this embodiment advantageously does not require the addition of base (and therefore is not susceptible to removal of any silyl protecting group). Particularly preferred is the hypervalent ethyl boronate complex (*ie* R is ethyl).

Group X may be an optionally ring substituted heterocyclic moiety. The heterocyclic moiety may contain one, two or three heterocyclic atoms which may be the same or different. Preferably the (or each) heterocyclic atom is selected from the group consisting of nitrogen, sulphur, oxygen, phosphorous and selenium, preferably the group consisting of nitrogen, oxygen and sulphur, particularly preferably the group consisting of nitrogen and sulphur. Preferably the heterocyclic moiety may be a 5- or 6-membered optionally ring substituted heterocyclic moiety.

By way of example, the heterocyclic moiety may be selected from the group consisting of optionally ring substituted thiophene, furan, pyridine, imidazole, isothiazole, isooxazole, pyran, pyrazine, pyridazine, pyrazole, pyridine, pyrimidine, triazole, oxadiazole, pyrrole, indazole, indole, indolizine, pyrrolizine, quinazoline, quinoline and

phenyl. Preferably the heterocyclic moiety is selected from the group consisting of optionally ring substituted thiophene and pyridine and particularly preferably is thiophene which may be substituted at the 3-position with an alkyl group (*e.g.* a C_{1-8}-alkyl such as a hexyl or octyl) or an aryl (*e.g.* a phenyl) group.

The counterion M may be a suitable metal counterion (*e.g.* Na or (preferably) Li).

The solid support may be any support compatible with the chosen parameters (*e.g.* solvent, temperature, reagents) and with chosen methods for monitoring the progress of the coupling reaction (*e.g.* IR or MAS NMR). Suitable solid supports may be surfaces, beads or fibres and will typically be polymeric including resins (preferably macroporous resins), tentagels or polystyrenes. The resins may be hydroxy functionalised (*e.g.* polyethyleneglycol based resins such as ARGOGEL™) or chloromethylated (*e.g.* chloromethylated polystyrene) to facilitate linking step (A).

In a preferred embodiment, step (A) comprises:

(A1) obtaining an immobilised germyl linking group on the solid support; and

(A2) linking the first monomer to the germanium of the immobilised germyl linking group.

The immobilised germyl linking group may be pre-prepared on the solid support or prepared *in situ* as desired. For example, an immobilised germyl linking group may be prepared from a solid support (*e.g.* resin) pre-functionalised with germanium. By way of example, a pre-prepared germane-containing styrenyl monomer may be copolymerised with styrene using a cross linker to give germanium functionalised polystyrene which may be straightforwardly activated for carrying out step (A2).

For step (A2), suitable reagents and conditions will be familiar to the skilled person and guidance may be found *inter alia* in Denat *et al*, Synthesis, 1992, 954-956 and Lukevics *et al*, J. Organomet. Chem., 1988, 20, 69-210.

The first monomer may be metallated (preferably lithiated) and reacted with the immobilised germyl linking grouping in step (A2). For this purpose, the immobilised germyl linking group has a suitable leaving group which is preferably chloride. The first monomer may be metallated in the chosen position (*e.g.* 2-, 3- or 2- and 5-positions of thiophene, pyrrole and furan and 2- or 3-positions of pyridine) whilst optionally protecting other positions. The chosen position may (for example) be metallated directly (*e.g.* lithiated directly using LDA) or by halogen-metal exchange of a halogen-substituted (*e.g.* bromo-substituted) first monomer (*e.g.* using n-BuLi). The germanium of the immobilised germyl linking group may be bound to an electronegative group to assist linking step (A2).

Alternatively the first monomer may be linked in step (A2) by cross-coupling. For this purpose, the first monomer may be halogenated. The first monomer may be halogenated in the chosen position (*e.g.* 2-, 3- or 2- and 5-positions of thiophene, pyrrole and furan and 2- or 3-positions of pyridine) whilst optionally protecting other positions. Such a cross-coupling reaction is typically mediated by a Pd(0) catalyst in the presence of a mild base

Step (A1) may comprise:

(A1') immobilising an immobilisable germyl linker on the solid support to form an immobilised germyl linking group;

Suitable immobilisable germyl linkers and methods for carrying out steps (A1), (A1') and (A2) will generally be familiar to the skilled person and guidance may be found in *inter alia* Spivey *et al*, Chem Commun., 1999, 835-836 and Spivey *et al*, J. Org. Chem., 2000, 65, 5253-5263.

Typically the immobilisable germyl linker is derivable from $GeCl_4$ and may be of formula:

$$ZGeR_2X$$

wherein:

each group R which may be the same or different is an alkyl (such as methyl, ethyl, butyl or *iso*-propyl), aryl, CF_3 or an electronegative group or precursor thereof;

X is H, a leaving group (such as $OCOCF_3$, OSO_3H or a halide (*e.g.* a chloride)) or a group MR'_n;

M is silicon, germanium, tin or boron;

R' is alkyl (e.g. C_{1-6}-akyl), aryl or alkoxy (*e.g.* C_{1-6}-alkoxy); and

Z is an immobilising group.

Where X is H or a group MR'_n, the first monomer may be linked in step (A2) via a cross-coupling reaction. For this purpose, the first monomer may be halogenated and reacted with the immobilised germyl linking group. Preferably M is silicon, germanium or boron.

Preferably one group R is an electronegative group which advantageously improves the efficiency of subsequent germanium cleavage (such as germyl-Stille type cleavage) during linking step (A2). The electronegative group may be a non-carbon bound group such as an oxygen or nitrogen bound group or a halide. Preferably the electronegative group is an alkoxy or amino group. A preferred alkoxy group R is OR^1 (wherein R^1 is a C_{1-6}-alkyl). A preferred amino group R is NR^2_2 (wherein R^2 is a C_{1-6}-alkyl).

Where one group R is a precursor to an electronegative group, step (A2) is preceded by:

(A0) converting the immobilisable germyl linker of formula $ZGeR_2X$ into an immobilisable germyl linker of formula $ZGeR_2X$ wherein one group R is an electronegative group.

This embodiment usefully permits a stable immobilisable germyl linker precursor to be converted into an immobilised germyl linking group which undergoes more efficient cleavage during step (A2). Step (A0) may be carried out oxidatively (*e.g.* by Germa-Polonovoski or Germa-Pummerer type reactions).

Immobilising group Z may be adapted to undergo Mitsunobu or Williamson type immobilisation to the solid support. Suitable immobilising groups Z include for example an

etherifiable group such as a hydroxylated group (*e.g.* a terminal hydroxy containing group) for immobilisation on a suitably functionalised resin by etherification. For this purpose, the solid (*e.g.* polymeric) support is functionalised (*e.g.* hydroxyl or chloromethyl functionalised). The suitability of immobilising group Z and the immobilisation conditions may be conveniently predetermined in solution by a Mitsunobu reaction using for example ethoxyethanol or by a Williamson reaction using for example 2-chloroethylethanol.

A solid support particularly useful for carrying out a process according to the invention is of formula X(OR-GeR^{1}R^2 Hal)n in which X is a high molecular weight material of low solubility in water and organic solvents, suitably a hydrocarbon resin substituted by alkoxy chains, for example polystyrene substituted by alkoxy, preferably propoxy or more preferably ethoxy or propoxy/ethoxy chains, R is a hydrocarbon group suitably having 1 to 12 and more preferably 3 to 10 carbon atoms, for example an alkyl, aryl group or arylalkyl group, the aryl group suitably comprising a benzene ring optionally substituted by alkyl groups, the Ge being preferably linked to an alkyl group, R^1 and R^2 individually being alkyl groups preferably having 1 to 6 carbon atoms and Hal representing a halide for example a bromide, iodide or preferably chloride atom and n being a large integer.

Protection/deprotection of the first monomer may facilitate the linking step (A). For example, a protecting group may be used to prevent unwanted lithiation at a specific position (*e.g.* the α-position) prior to step (A2). Although any suitable protecting group may be used, a trimethylsilyl, TMS, or tert. butyl dimethylsilyl, TBDMS, group is preferred and may be removed with familiar reagents such as a base *e.g.* K_3PO_4 or CsF prior to coupling step (B).

The invention thus provides a method for preparing a conjugated molecule comprising a first monomer coupled to a second monomer, said method comprising:

(i) linking the first monomer to a solid support via the germanium atom of a germyl linking group;

(ii) coupling the first monomer to the second monomer in a coupling position to form a bound conjugated molecule, wherein the second monomer has a protecting group in a non-coupling position;

(iii) optionally sequentially coupling a third, fourth....and nth monomer to the second, third and (n-1)th monomer respectively;

(iv) removing the protecting group; and

(v) *ipso*-degermylation to release the bound conjugated molecule.

The present invention will now be described in a non-limitative sense with reference to the following Examples and the Figures in which:

Figure 1 illustrates the resin/linkers adopted in the prior art by Fréchet **1** and Bäuerle **2**;
Figure 2 illustrates the germyl linker **3** used in Example 1 relating to a solution phase model of a solid phase synthesis;

Figure 3 illustrates the envisaged key steps in the iterative solid phase synthesis of an oligothiophene;

Figure 4 illustrates linking of a protected thiophene monomer to the germyl linker (**4** to $\mathbf{5}^{1}$);

Figure 5 illustrates a proposed deprotection protocol ($\mathbf{5}^{1}$ to $\mathbf{6}^{1}$);

Figure 6 illustrates a proposed iodination protocol ($\mathbf{6}^{1}$ to $\mathbf{7}^{1}$);

Figure 7 illustrates a proposed coupling protocol ($\mathbf{7}^{1}$ to $\mathbf{5}^{2}$);

Figure 8 illustrates a complete iterative cycle, including 'double coupling' ($\mathbf{5}^{2}$ to $\mathbf{5}^{3}$);

Figures 9 illustrates potential products of cleavage protocols from the germyl linker ($\mathbf{5}^{n+1}$ to $\mathbf{8}^{n+1}$)

Figure 10 illustrates schematically the preparation of block oligomers.

Example 1

Example 1 relates to a solution phase model of the solid phase synthesis of a high purity thiophene oligomer having well-defined regiochemistry using a germyl linker. Assembly of the oligomer is a stepwise process in which each monomer unit is added sequentially through repetitive transition metal mediated coupling to obtain highly pure and well-defined structures.

In order to compare materials obtained by the present method with conventional methods, it was decided to investigate the solution phase synthesis of hexylthiophene oligomers using a germyl linker **3** (see Figure 2) as a model for a solid phase synthesis which is outlined in Figure 3 and whose steps may be summarised as:

Step 1: attachment of the first TMS blocked monomer,

Step 2: to the cleavage of the TMS blocking group,

Step 3: conversion to an -iodide coupling precursor,

Step 4: cross-coupling of a second TMS blocked monomer,

Step 5: removal of the oligomer from the germanium-based linker.

Steps 2, 3, and 4 represent the repetitive steps for the oligomer build-up. The role of the TMS group is to block the terminal -position of the iterated oligomer allowing steps 3-4 to be repeated in a double-coupling cycle so as to drive any unreacted iodide and any uniodinated/deiodinated material through to iterated product.

Step 1: (Figure 4)

Thiophene $\mathbf{5}^{1}$ was prepared by transmetalation of linker model **3** with lithiated thiophene **4** in 53% yield. Here, the TMS protecting group ensures that none of the undesired alternate -lithiated thiophene is formed and moreover, in the context of **SPS**, would allow immobilization to be driven to completion by repeat transmetalation.

Step 2: (Figure 5)

Cleavage of the TMS protecting group in thiophene 5^1 was achieved using CsF in DMF at 60°C and gave germylthiophene 6^1 almost quantitatively with no detectable cleavage of the germyl linker.

Step 3: (Figure 6)

-Iodination was achieved by the use of excess *n*-BuLi at –50°C followed by treatment with excess 1,2-diiodoethane in the dark. Conversion of germylthiophene 6^1 to the corresponding iodothiophene 7^1 under these conditions was achieved in 98% yield.

Step 4: (Figure 7)

Iodothiophene 7^1 was coupled using a novel 'base-free' Suzuki-type cross-coupling protocol to triethylborate salt **10**. This salt is obtained as an easily handled white powder by direct evaporation of volatiles following lithiation/transmetalation of thiophene **4** with *n*-BuLi/$B(OEt)_3$ at –50°C in THF. Using 5mol% $Pd(PPh_3)_4$ in DMF at 60°C *in the absence of added base* this salt cross-couples with iodothiophene 7^1 to give dithiophene 5^2 in 90% yield. No *ipso*-protodesilylation of the TMS group occurs under these conditions.

Double-coupling (Steps 3-4, repeated):

Successful double-coupling requires the TMS blocking group itself to be inert to step 3 and therefore sufficiently robust to enable iodination of any uncoupled and/or deiodinated material remaining following coupling. Analysis by ^{1}H NMR of the 'crude' reaction mixture following a cross-coupling between iodothiophene 7^1 and an excess of triethyborate salt **10** (Figure 7) reveals, in addition to >90% cross-coupled product 5^2, small amounts of both unreacted iodothiophene 7^1 and deiodinated thiophene 6^1. Therefore, to validate the concept of double-coupling we subjected this material to a repeat -iodination/coupling cycle (steps 3-4) and re-examined the reaction mixture. Following this simulated double-coupling, by-products 7^1 and 6^1 can no longer be detected by ^{1}H NMR.

A second iteration (n = 2, steps 2-4, including simulated double-coupling) was also performed on dithiophene 5^2 yielding trithiophene 5^3 with analogous results (Figure 8).

Step 5: (Figure 9)

There are a number of options available for step 5 depending on the intended use of the cleaved oligomer. Protocols that result in the cleavage of both symmetrically end-functionalised and -telechelic oligomers with various useful end-functionality are possible.

Cleavage by an electrophile E^+ (*e.g.* H^+, I^+, Br^+, Cl^+, F^+, NO^+, NO_2^+, SO_3^+, RCO^+, RSO_2^+, $BHal_2^+$(*e.g.* BCl_2^+) or $B(OH)_2^+$) results in electrophilic *ipso*-degermylation to introduce substituent Y^E leaving the TMS blocking group intact (Y = RMe_2Ge to Y = Y^E; Z = TMS). Under more forcing conditions both electrophilic *ipso*-degermylation and *ipso*-desilylation occurs giving symmetrically end-functionalised oligomer (Y = RMe_2Ge to Y =

Y^E and Z = TMS to Z = Z^E where Y^E = Z^E). The use of two different electrophiles sequentially gives an -telechelic oligomer (**8**$^{n+1}$, Y = Y^E and Z = Z^E where Y^E Z^E). The use of an electrophile RCO^+ in a Friedel-Crafts type *ipso*-degermylation is particularly attractive as subsequent reduction of the resulting ketone carbonyl to a methylene group (using for example $LiAlH_4$-$AlCl_3$) leaves an alkyl end-functionalised conjugated molecule. These are known to have favourable electronic properties (see for example Katz, Acc. Chem. Res., 2001, 45, 11).

Cleavage by a germyl-Stille type cross-coupling protocol introduces a C-C bond in place of the C-Ge bond leaving the TMS blocking group intact (Y = RMe_2Ge to Y = Y^{CC}; Z = TMS). Potential cross-coupling partners for this type of cleavage are substrates that can undergo oxidative insertion of Pd(0) to yield an active Pd(II) intermediate as in a standard Stille-type cross-coupling. These include aryl, heteroaryl, benzyl, allyl, propargyl, and alkynyl halides (*e.g.* I, Br, Cl), sulfonate esters (*e.g.* OSO_2CF_3, OSO_2CH_3, OSO_2p-Tol), and diazonium salts (N_2^+). Cleavage in this fashion could be followed by electrophilic *ipso*-desilylayion as described above (Z = TMS to Z = Z^E) or by nucleophilic *ipso*-protodesilylation (*cf* step 2, *e.g.* Figure 5) with a base (e.g. CsF, K_3PO_4) to introduce a hydrogen in place of the TMS blocking group (Z = TMS to Z = H).

Treatment with a base (*e.g.* CsF, K_3PO_4) to effect nucleophilic *ipso*-protodesilylation (Z = TMS to Z = H) could also be performed *prior* to cleavage. Such cleavage by an electrophile E^+, or by sequential use of two electrophiles, as described above, could again result in -telechelic or symmetrical oligomers by electrophilic *ipso*-degermylation without or with subsequent electrophilic substitution at the other terminus [(Y = RMe_2Ge to Y = Y^E; Z = H) or (Y = RMe_2Ge to Y = Y^E and Z = H to Z = Z^E where Y^E = Z^E or Y^E Z^E]. Similarly, such cleavage by a Germyl-Stille type cross-coupling, as described above, could result in , -telechelic oligomers (Y = RMe_2Ge to Y = Y^{CC}; Z =H) which could undergo subsequent electrophilic substitution at the other terminus (Z = H to Z = Z^E).

In this manner a wide range of usefully end-functionalised oligomers can be produced which may have useful electroactive properties in their own right and/or be valuable substrates for subsequent incorporation into more complex structures (e.g. block co-oligomers).

Preparation of block co-oligomers (Figure 10)

An oligoheterocyclic block prepared as described above is in an advantageous form for incorporation into a block co-oligomeric structure. Block coupling could be achieved by a number of possible protocols:

Type 1. by the coupling of oligoheterocyclic blocks in place of the single thiophene unit **9** by analogy with the iterative cycle;

Type 2. by direct germyl-Stille type cross coupling off the linker;

Type 3. by a Suzuki, Kharasch (*e.g.* McCullough) Stille, or Negishi,-type cross-coupling reaction between an appropriate halo-functionalised block and a metalated block in solution. Both types of coupling partner for this mode of block coupling can be prepared by appropriate electrophilic *ipso*-degermylation of oligoheterocyclic blocks prepared as described above.

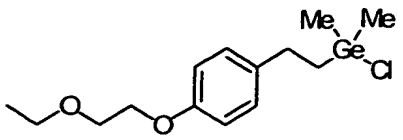
These generic possibilities are illustrated by way of example in Figure 10.

Experimental Procedures

All reactions were performed under anhydrous conditions and an atmosphere of nitrogen in flame-dried glassware. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogenous materials, unless otherwise indicated.

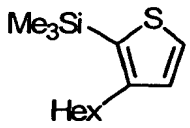
Solvents and reagents: All solvents were distilled before use. 'Petrol' refers to the fraction of light petroleum-ether boiling between 40 – 60°C. Commercial grade solvents used for flash chromatography were distilled before use. Anhydrous solvents were obtained as follows: DMF: Stirred over $MgSO_4$ under nitrogen for 24h, distilled under reduced pressure, and stored over molecular sieves (4Å) under nitrogen. $MeNO_2$: Distilled from CaH_2 under nitrogen immediately prior to use. THF and Et_2O: Distilled from sodium/benzophenone ketyl under nitrogen immediately prior to use. 'Degassed' refers to solutions that have been subjected to three successive freeze-thaw cycles on a nitrogen/high-vacuum line. All chemicals were handled in accordance with COSHH regulations. All reagents were used as commercially supplied. ***Chromatography:*** Flash chromatography was carried out using Merck Kiesegel 60 F_{254} (230-400 mesh) silica gel. Only distilled solvents were used as eluents. Thin layer chromatography (TLC) was performed on Merck which were visualised either by quenching of ultraviolet fluorescence (λ_{max} = 254 nm) or by charring with 10% $KMnO_4$ in 1M H_2SO_4. ***Infra red spectra:*** These were recorded as thin films, nujol mulls, or as solutions in $CHCl_3$, on a Perkin-Elmer Paragon 1000 Fourier transform spectrometer. Only selected absorbencies (λ_{max}) are reported. ***^{1}H NMR spectra***: These were recorded at 250 MHz on a Bruker AM-250 instrument, and at 300MHz and 400MHz on Varian Inova-300 and -400 instruments respectively. Chemical shifts (δ_H) are quoted in parts per million (ppm), referenced to the appropriate residual solvent peak. Coupling constants (*J*) are reported to the nearest Hz. ***^{13}C NMR spectra:*** These were recorded at 63 MHz on a Bruker AM-250 instrument, and at 100MHz on a Varian Inova-300. Chemical shifts (°C) are quoted in ppm, referenced to the appropriate solvent peak. ***Mass spectra:*** Low resolution mass spectra (m/z) were recorded on either a VG platform or VG prospec spectrometers, with only molecular ions (M^+ or MH^+), and major peaks being reported with intensities quoted as percentages of the base peak. High Resolution Mass Spectrometry (HRMS) measurements are valid to ±5 ppm.

{2-[4-(2-Ethoxy-ethoxy)-phenyl]-ethyl}-dimethyl-germyl-chloride 3



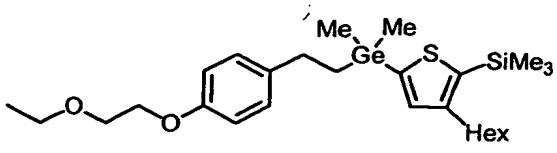
Tin(IV)chloride (1.50mL, 12.8mmol) was added drop-wise to a solution of {2-[4-(2-ethoxy-ethoxy)-phenyl]-ethyl}-trimethyl-germane (421mg, 1.4mmol) in nitromethane (2mL) at RT to give a pink solution. The reaction mixture was then heated at 50°C for 16h. Volatiles were then removed by distillation (90°C, 0.5mmHg) to leave chlorodimethylgermane **3** as a brown oil (440mg, 91%).); ^{1}H NMR ($CDCl_3$): δ 0.59 (s, 6H), 1.24 (t, J = 7, 3H), 1.49 (t, J = 8, 2H), 2.80 (t, J = 8, 2H), 3.59 (q, J = 7, 2H), 3.77 (t, J = 5, 2H), 4.10 (t, J = 6, 2H), 6.85 (d, J = 8.5, 2H), 7.10 (d, J = 8, 2H); MS (EI+) *m/z* 332 (M^+). HRMS (EI+) calcd. for $C_{14}H_{23}ClGe^{74}O_2$ (M) 332.0598, found 332.0586.

(3-Hexyl-thiophen-2-yl)-trimethyl-silane 4



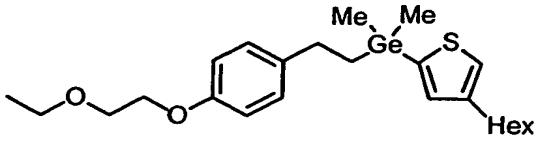
A solution of *n*-BuLi (0.787mL, 2.2M, 1.73mmol) in hexanes was added drop-wise to a degassed solution of 2-bromo-3-hexylthiophene[1] (387mg, 1.57mmol) in THF (3mL) at -78°C. The mixture was stirred for 40min at this temperature, and then trimethylchlorosilane (0.600mL, 4.71mmol) added drop-wise at -78°C. The resulting mixture was stirred for 1hr at this temperature, warmed to RT and stirred for a further 1hr. After quenching with sat. NH_4Cl (aq) (100mL), the mixture was extracted with Et_2O (3×100mL), the combined organic extracts dried ($MgSO_4$) and the solvent removed *in vacuo*. Purification by flash chromatography (pentane) gave silylthiophene **4** as a colourless oil (329mg, 87%). R_f 0.85 (pentane); ^{1}H NMR ($CDCl_3$): δ 0.03 (s, 9H), 0.58 (t, J = 6.5, 3H), 0.95-1.10 (m, 6H), 1.22-1.31 (m, 2H), 2.36 (t, J = 8, 2H), 6.73 (d, J = 4.5, 1H), 7.14 (d, J = 4.5, 1H); MS (CI+) *m/z* 240 (M^+). HRMS (CI+) calcd. for $C_{13}H_{24}SiS$ (M) 240.1368, found 240.1361.

[5-({2-[4-(2-Ethoxy-ethoxy)-phenyl]-ethyl}-dimethyl-germanyl)-3-hexyl-thiophen-2-yl)-trimethyl-silane 5[1]



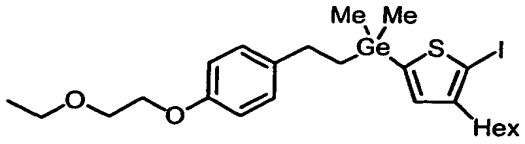
A solution of LDA (0.315mL, 2.0M, 0.63mmol) in hexanes/THF/ethylbenzene was added drop-wise to a degassed solution of silylthiophene **4** (144mg, 0.60mmol) in THF (2mL) at -78°C. This solution was stirred for 40min at this temperature, and then transferred by cannula to a degassed solution of chlorodimethylgermane **3** (100mg, 0.30mmol) in THF (1mL) at -78°C. The resulting mixture was stirred for 1hr at this temperature, warmed to RT and stirred for a further 1hr. After quenching with sat. NH_4Cl (aq) (50mL), the mixture was extracted with Et_2O (3×50mL), the combined organic extracts dried ($MgSO_4$) and the solvent removed *in vacuo*. Purification by flash chromatography (petrol/EtOAc, 9/1) gave silylthiophenedimethylgermane **5**[1] as a yellow oil (86.0mg, 53%). R_f 0.61 (9/1, petrol/EtOAc); ^1H NMR ($CDCl_3$) δ 0.33 (s, 9H), 0.39 (s, 6H), 0.86 (t, J = 7.5, 3H), 1.24 (t, J = 7, 3H), 1.24-1.42 (m, 8H), 1.54-1.62 (m, 2H), 2.63-2.72 (m, 4H), 3.59 (q, J = 7, 2H), 3.77 (t, J = 5.5, 2H), 4.09 (t, J = 6, 2H), 6.83 (d, J = 8.5, 2H), 7.06 (s, 1H), 7.07 (d, J = 8, 2H); ^{13}C NMR ($CDCl_3$) δ -2.18 (2xq), 0.46 (3xq), 14.10 (q), 15.19 (q), 19.11 (t), 22.65 (t), 29.56 (t), 30.09 (t), 31.10 (t), 31.77 (t), 31.98 (t), 66.84 (t), 67.50 (t), 69.05 (t), 114.55 (2xd), 128.72 (2xd), 136.45 (d), 136.79 (s), 137.59 (s), 144.24 (s), 151.46 (s), 156.96 (s); IR (neat) 2928, 2858, 1688, 1611, 1584, 1511, 1246, 1125, 839 cm^{-1}; MS (EI+) *m/z* 536 (M^+). HRMS (EI+) calcd. for $C_{27}H_{46}O_2SiSGe^{74}$ (M) 536.2200, found 536.2214.

{2-[4-(2-Ethoxy-ethoxy)-phenyl]-ethyl}-(4-hexyl-thiophen-2-yl)-dimethyl-germane 6[1]



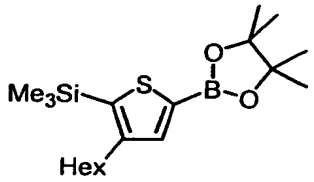
To TMS protected germylthiophene **5**[1] (5.7mg, 0.011mmol) in DMF (1mL) was added ceasium fluoride (8.1mg, 0.053mmol) and the mixture left to stir for 24hrs at 60°C. The reaction mixture was partitioned between Et_2O (40mL) and water (75ml) and the Et_2O layer extracted with water (3x40ml). The organic layer was dried ($MgSO_4$), the solvent removed *in vacuo* and the residue purified by flash chromatography (petrol/EtOAc, 9/1) to give germyldithiophene **6**[1] as a brown oil (4.8mg, 97%). R_f 0.38 (petrol/EtOAc, 9/1); ^1H NMR ($CDCl_3$): δ 0.38 (s, 6H), 0.88 (t, J = 7, 3H), 1.23 (t, J = 7, 3H), 1.25–1.30 (m, 8H), 1.54–1.62 (m, 2H), 2.62 (t, J = 8, 2H), 2.67 (t, J = 8.5, 2H), 3.59 (q, J = 7, 2H), 3.77 (t, J = 5.5, 2H), 4.09 (t, J = 5.5, 2H), 6.83 (d, J = 8, 2H), 6.96 (s, 1H), 7.06 (s, 1H), 7.11 (d, J = 8, 2H); ^{13}C NMR ($CDCl_3$) δ -2.29 (2xq), 14.12 (q), 15.19 (q), 19.10 (t), 22.63 (t), 29.16 (t), 30.09 (2xt), 30.67 (t), 31.71 (t), 66.84 (t), 67.52 (t), 69.05 (t), 114.57 (2xd), 124.51 (d), 128.72 (2xd), 134.51 (d), 136.75 (s), 139.57 (s), 144.48 (s), 156.96 (s); IR (neat) 2927, 2857, 1611, 1511, 1246, 1126 cm^{-1}; MS (EI+) *m/z* 464 (M^+); HRMS (EI+) calcd. for $C_{24}H_{38}Ge^{74}O_2S$ (M) 464.1804, found 464.1798.

{2-[4-(2-Ethoxy-ethoxy)-phenyl]-ethyl}-(4-hexyl-5-iodo-thiophen-2-yl)-dimethyl-germane 7[1]



A solution of *n*-BuLi (2.21mL, 1.5M, 3.30mmol) in hexanes was added drop-wise to a degassed solution of germylthiophene **6**[1] (512mg, 1.10mmol) in THF (3mL) at -78°C. After stirring for 40min at this temperature, a solution of degassed 1,2-diiodoethane (1.56g, 5.52mmol) in THF (2mL) was added by cannula at -78°C. The resulting mixture was stirred in the dark for 1hr at this temperature, warmed to RT and stirred for a further 1hr. The reaction mixture was partitioned between sat. $Na_2S_2O_3$ (aq) (200mL) and Et_2O (100ml), extracted with Et_2O (2×100mL), the organics combined and then dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue purification by flash chromatography (petrol/EtOAc, 9/1) to give germylthiopheneiodide **7**[1] as a yellow oil (632mg, 98%). R_f 0.41 (petrol/EtOAc, 9/1); ^{1}H NMR ($CDCl_3$): δ 0.37 (s, 6H), 0.88 (t, J = 6.5, 3H), 1.23 (t, J = 7, 3H), 1.25–1.31 (m, 8H), 1.53–1.56 (m, 2H), 2.53 (t, J = 8, 2H), 2.66 (t, J = 8, 2H), 3.59 (q, J = 7, 2H), 3.77 (t, J = 5.5, 2H), 4.09 (t, J = 6, 2H), 6.75 (s, 1H), 6.83 (d, J = 8.5, 2H), 7.07 (d, J = 8, 2H); ^{13}C NMR ($CDCl_3$) δ -2.30 (2xq), 14.13 (q), 15.20 (q), 19.06 (t), 22.63 (t), 29.05 (t), 30.02 (t), 30.14 (t), 31.65 (t), 31.91 (t), 66.85 (t), 67.51 (t), 69.05 (t), 77.91 (s), 114.58 (2xd), 128.73 (2xd), 133.86 (d), 136.41 (s), 145.61 (s), 148.17 (s), 157.02 (s); IR (neat) 2928, 2856, 1611, 1584, 1510, 1455, 1246, 1125 cm^{-1}; MS (EI+) *m/z* 590 (M^+). HRMS (ES+) calcd. for $C_{24}H_{38}O_2SGe^{74}$ (MH) 591.0849, found 591.0870.

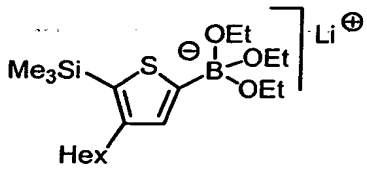
2-(4-Hexyl-5-trimethylsilanyl-thiophen-2-yl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane 8



A solution of LDA (0.690mL, 2.0M, 1.38mmol) in hexanes/ethylbenzene/THF was added drop-wise to a degassed solution of TMS thiophene **4** (166mg, 0.69mmol) in THF (2mL) at -50°C. After stirring for 40min at this temperature, a degassed solution of 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (334mg, 1.79mmol) in THF (2mL) was added by cannula at -78°C. The resulting mixture was stirred for 30min at this temperature, warmed to RT and stirred for a further 15min. The reaction mixture was cooled to 0°C and anhydrous HCl in Et_2O (1.79ml, 1.0M, 1.79mmol) added. The mixture was left to stir at this

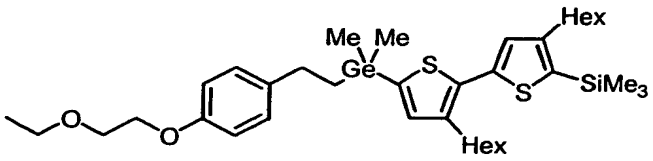
temperature for 15min and then allowed to warm to RT. The solvent was removed *in vacuo* and the residue taken up in dry Et_2O. The solution was passed through a pad of dry celite, dried ($MgSO_4$) and the solvent removed *in vacuo*. The residue was purified by flash chromatography (petrol/EtOAC, 19/1) to give thiophene pinacolato boronic ester as a courless oil (131mg, 52%). ^1H NMR ($CDCl_3$): δ 0.03 (s, 9H), 0.58 (t, J = 7, 3H), 0.94-1.02 (m, 6H), 1.03 (s, 12H), 1.27 (m, 2H), 2.36 (t, J = 8, 2H), 7.26 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 0.23 (3xq), 14.07 (q), 22.58 (t), 24.74 (4xq), 29.43 (t), 31.00 (t), 31.76 (2xt), 83.97 (2xs), 140.01 (d), 141.46 (s), 151.64 (s) (absent: SCB); MS (EI+) *m/z* 367 (M^+).

(4-Hexyl-5-trimethylsilanyl-thiophen-2-yl)-triethylborate lithium salt 9



A solution of *n*-BuLi (0.298mL, 1.5M, 0.45mmol) in hexanes was added drop-wise to a solution of silylthiophene **4** (97.6mg, 0.41mmol) in THF (2mL) at -50°C and stirred for 40min at this temperature. To this was added triethylborate (0.207mL, 1.22mmol) drop-wise at -50°C. The resulting mixture was stirred for 1hr at this temperature, warmed to RT and stirred for a further 30min. The solvent was then removed *in vacuo* to give the triethylborate lithium salt **9** as a white powder. mp 95-98°C; ^1H NMR ($CDCl_3$): δ 0.33 (s, 9H), 0.88 (t, J = 6.5, 3H), 1.17-1.58 (m, 17H), 2.66 (t, 2H), 4.14 (q, J = 7, 6H), 7.46 (s, 1H).

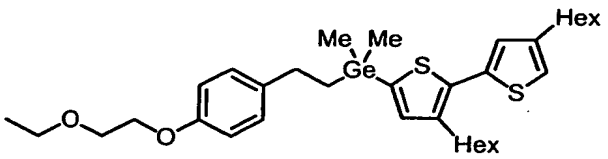
[5'-({2-[4-(2-Ethoxy-ethoxy)-phenyl]-ethyl}-dimethyl-germanyl)-4,3'-dihexyl-[2,2']bithiophenyl-5-yl]-trimethyl-silane 5[2]



To a degassed solution of triethylborate salt **9** (63.0mg, 0.101mmol) and germylthiopheneiodide **7**[1] (30.0mg, 0.051mmol) in THF (1mL) at -78°C was added $Pd(PPh_3)_4$ (6.0mg, 0.0051mmol) and the resulting mixture stirred at 60°C for 24hr. The reaction mixture was partitioned between water (100mL) and Et_2O (50ml), extracted with Et_2O (2×50mL) and the organics combined and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue purification by flash chromatography (petrol/EtOAc, 9/1) to give silyl protected germyldithiophene **5**[2] as a yellow oil (29.0mg, 90%). R_f 0.50 (petrol/EtOAc, 9/1); ^1H NMR ($CDCl_3$): δ 0.05 (s, 9H), 0.10 (s, 6H), 0.53-0.62 (m, 6H), 0.94 (t, J = 7, 3H),

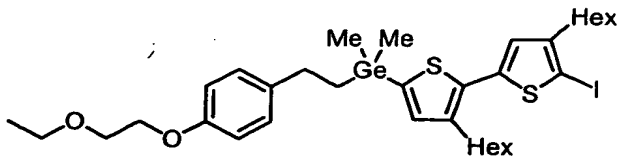
0.94-1.08 (m, 14H), 1.28-1.34 (m, 4H), 2.30-2.48 (m, 6H), 3.30 (q, J = 7, 2H), 3.47 (t, J = 4.5, 2H), 3.79 (t, J = 4.5, 2H), 6.54 (d, J = 8.5, 2H), 6.63 (s, 1H), 6.74 (s, 1H), 7.80 (d, J = 8.5, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ -2.34 (2xq), 0.43 (3xq), 14.08 (2xq), 15.16 (q), 19.08 (t), 22.62 (2xt), 29.20 (t), 29.31 (t) 29.39, (t), 30.07 (t), 30.70 (t), 31.48 (t), 31.64 (t), 31.70 (t), 31.77 (t), 66.82 (t), 67.53 (t), 69.03 (t), 114.58 (2xd), 128.73 (2xd), 128.79 (d), 132.61 (s), 135.63 (s), 136.11 (d), 136.67 (s), 137.97 (s), 140.19 (s), 140.34 (s), 150.68 (s), 156.97 (s); IR (neat) 2956, 2928, 2858, 1732, 1611, 1584, 1511, 1236 cm^{-1}; MS (EI+) *m/z* 702 (M^+). HRMS (ES+) calcd. for $C_{37}H_{61}O_2SiS_2Ge^{74}$ (MH) 703.3094, found 703.3089.

(3,4'-Dihexyl-[2,2']bithiophenyl-5-yl)-{2-[4-(2-ethoxy-ethoxy)-phenyl]-ethyl}-dimethyl germane 6[2]



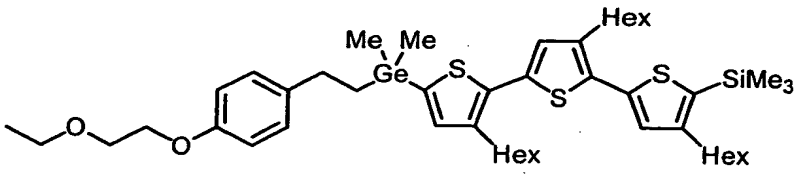
To TMS protected germyldithiophene **5**[2] (60.0mg, 0.086mmol) in DMF (1mL) was added ceasium fluoride (63.4mg, 0.42mmol) and the mixture left to stir for 24hrs at 60°C. The reaction mixture was partitioned between Et_2O (50mL) and water (100ml) and the Et_2O layer extracted with water (3x50ml). The organic layer was dried ($MgSO_4$), the solvent removed *in vacuo* and the residue purified by flash chromatography (petrol/EtOAc, 9/1) to give germyldithiophene **6**[2] as a brown oil (54.0mg, 99%). R_f 0.40 (9/1, petrol/EtOAc); ^{1}H NMR ($CDCl_3$): δ 0.40 (s, 6H), 0.85-0.90 (m, 6H), 1.23 (t, J = 7H, 3H), 1.20-1.33 (m, 14H), 1.56-1.62 (m, 4H), 2.59 (t, J = 7.5, 2H), 2.66-2.76 (m, 4H), 3.59 (q, J = 7, 2H), 3.77 (t, J = 4.5, 2H), 4.09 (t, J = 5, 2H), 6.83 (d, J = 8.5, 2H), 6.86 (s, 1H), 6.92 (s, 2H), 7.08 (d, J = 8.5, 2H); ^{13}C NMR (400 MHz, $CDCl_3$) δ -2.32 (2xq), 14.13 (2xq), 15.20 (q), 19.07 (t), 22.65 (2xt), 29.03 (t), 29.18 (t), 29.37 (t), 30.08 (t), 30.41 (t), 30.54 (t), 30.80 (t), 31.68 (2xt), 66.85 (t), 67.49 (t), 69.05 (t), 114.55 (2xd), 119.71 (d), 126.93 (d), 128.74 (2xd), 135.61 (s), 136.09 (d), 136.65 (s), 138.06 (s), 140.35 (2xs), 143.53 (s), 156.97 (s); IR (neat) 2927, 2857, 1728, 1611, 1510, 1457, 1246, 1125 cm^{-1}; MS (EI+) *m/z* 630 (M^+). HRMS (CI+) calcd. for $C_{34}H_{52}O_2S_2Ge^{74}$ (M) 630.2621, found 630.2642.

(3,4'-Dihexyl-5'-iodo-[2,2']bithiophenyl-5-yl)-{2-[4-(2-ethoxy-ethoxy)-phenyl]-ethyl}-dimethyl germane 7[2]



A solution of *n*-BuLi (0.060mL, 2.5M, 0.149mmol) in hexanes was added drop-wise to a degassed solution of germyldithiophene **6**[2] (19.0mg, 0.030mmol) in THF (1mL) at -78°C. After stirring for 40min at this temperature, a degassed solution of 1,2-diiodoethane (67.2mg, 0.238mmol) in THF (1mL) was added by cannula at -78°C. The resulting mixture was stirred in the dark for 1hr at this temperature, warmed to RT and stirred for a further 1hr. The reaction mixture was partitioned between sat. $Na_2S_2O_3$ (aq) (50mL) and Et_2O (50ml), extracted with Et_2O (2×50mL), the organics combined and then dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue purification by flash chromatography (petrol/EtOAc, 9/1) to give germyldithiopheneiodide **7**[2] as a yellow oil (23.1mg, 98%). R_f 0.42 (9/1, petrol/EtOAc); ^1H NMR ($CDCl_3$): δ 0.33 (s, 6H), 0.78-0.85 (m, 6H), 1.17 (t, J = 7H, 3H), 1.17-1.27 (m, 14H), 1.50-1.54 (m, 4H), 2.46 (t, J = 7.5, 2H), 2.58-2.67 (m, 4H), 3.53 (q, J = 7, 2H), 3.71 (t, J = 5, 2H), 4.03 (t, J = 5, 2H), 6.68 (s, 1H), 6.77 (d, J = 8.5, 1H), 6.85 (s, 1H), 7.02 (d, J = 8.5, 2H); ^{13}C NMR (400 MHz, $CDCl_3$) δ -2.43 (2xq), 14.10 (q), 14.20 (q), 15.17 (q), 19.03 (t), 22.62 (2xt), 28.90 (t), 29.15 (t), 29.31 (t), 29.95 (t), 30.05 (t), 30.76 (t), 31.65 (2xt), 32.35 (t), 66.84 (t), 67.48 (t), 69.03 (t), 73.63 (q), 114.55 (2xd), 126.20 (d), 128.72 (2xd), 135.57 (s), 136.04 (d), 136.53 (s), 138.81 (s), 140.90 (s), 141.06 (s), 147.48 (s), 156.98 (s); IR (neat) 2928, 2857, 1728, 1611, 1511, 1455, 1125 cm^{-1}; MS (EI+) *m/z* 756 (M^+). HRMS (EI+) calcd. for $C_{34}H_{51}O_2S_2Ge^{74}I$ (M) 756.1587, found 756.1571.

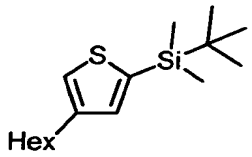
[5"-({2-[4-(2-Ethoxy-ethoxy)-phenyl]-ethyl}-dimethyl-germanyl)-4,3',3"-trihexyl-[2,2';5'2"]terthiophen-5-yl]-trimethyl-silane 5[3]



To a degassed solution of triethylborate salt **9** (118mg, 0.30mmol) and germyldithiopheneiodide **7**[2] (29.7mg, 0.039mmol) in THF (1mL) at -78°C was added $Pd(PPh_3)_4$ (6.0mg, 0.0051mmol) and the resulting mixture stirred at 60°C for 24hr. The reaction mixture was partitioned between water (100mL) and Et_2O (50ml), extracted with Et_2O (2×50mL) and the organics combined and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue purification by flash chromatography (petrol/EtOAc, 9/1) to give silyl protected germyltrithiophene **5**[3] as a yellow oil (31.6mg, 93%). R_f 0.52 (petrol/EtOAc, 9/1); ^1H NMR ($CDCl_3$): δ 0.25 (s, 9H), 0.31 (s, 6H), 0.75-0.83 (m, 9H), 1.14 (t, J = 7, 3H), 1.19-1.25 (m, 20H), 1.47-1.55 (m, 6H), 2.50-2.70 (m, 8H), 3.50 (q, J = 6.5, 2H), 3.68 (t, J = 5, 2H), 4.00 (t, J = 5, 2H), 6.74 (d, J = 9, 2H), 6.82 (s, 1H), 6.83 (s, 1H), 6.96(s, 1H), 7.00 (d, J = 9, 2H); IR (neat) 2928, 2858, 1729, 1611, 1584, 1511, 1456, 1248, 839 cm^{-1}; MS

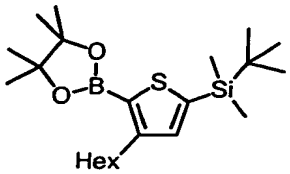
(ES+) *m/z* 869 (MH^+). HRMS (ES+) calcd. for $C_{47}H_{74}O_3S_2Ge^{74}I$ (MH) 869.3910, found 869.3901.

tert-Butyl-(4-hexyl-thophen-2-yl)-dimethyl-silane 10



A solution of LDA (3.12mL, 2.0M, 6.24mmol) in hexanes/ethylbenzene/THF was added drop-wise to a degassed solution of 3-hexyl-thiophene (1.00g, 5.94mmol) in THF (10mL) at -50°C to give an orange solution. After stirring for 40min at this temperature, a degassed solution of *tert*-butyldimethylsilyl chloride (1.34g, 0.89mmol) in THF (5mL) was added by cannula at -50°C. The resulting mixture was warmed to -40°C, stirred for 30min at this temperature, warmed to RT and stirred for a further 40min to give a yellow solution. After quenching with sat. NH_4Cl (aq) (50mL), the mixture was extracted with Et_2O (3×50mL), the combined organic extracts dried ($MgSO_4$) and the solvent removed *in vacuo*. Purification was initially by vacuum distillation (105°C, 10^{-3}Torr) to remove starting material and then by reverse phase HPLC (MeOH/H_20, 19/1) to give silylthiophene **10** as a colorless oil (1.05g, 63%). ^1H NMR ($CDCl_3$): δ 0.27 (s, 6H), 0.87 (t, J = 7.5, 3H), 0.90 (s, 9H), 1.24-1.30 (m, 6H), 1.61 (t, J = 8, 2H), 2.62 (t, J = 8, 2H), 7.15 (s, 1H), 7.25 (s, 1H); ^{13}C NMR ($CDCl_3$) δ -4.88 (2xq), 14.16 (q), 16.87 (s), 22.67 (t), 26.39 (3xq), 29.14 (t), 30.02 (t), 30.70 (t), 31.73 (t), 125.42 (d), 136.63 (d), 136.91 (s), 144.47 (s); IR (neat) 2953, 2925, 2855, 1462, 1406, 1361, 1249, 1198, 1008, 938, 832 cm^{-1}; MS (EI+) *m/z* 282 (M^+); HRMS (EI+) calcd. for $C_{16}H_{30}SSi$ (M) 282.1838, found 282.1827; Anal. calcd. for $C_{16}H_{30}SSi$: C 68.01, H 10.70, S 11.35, found C 68.45, H 11.04, S 11.45; HPLC purity 100.0%.

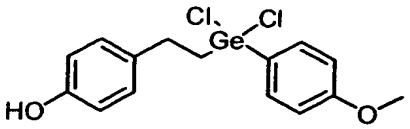
2-[5-(_tert_-Butyl-dimethyl-silanyl)-3-hexyl-thiophen-2-yl]-4,4,5,5-tetramethyl-[1,2,3]dioxaboralane 11



A solution of LDA (1.33mL, 2.0M, 2.66mmol) in hexanes/ethylbenzene/THF was added drop-wise to a solution of silylthiophene **10** (501mg, 1.77mmol) in THF (5mL) at -50°C and then warmed to -40°C give an orange solution. After stirring for 40min at this temperature the reaction was cooled to -50°C and a solution of 2-isopropoxy-4,4,5,5-tetramethyl-

[1,3,2]dioxaborolane (162mg, 0.87mmol) in THF (1mL) (x3) was added drop-wise by cannula. The resulting mixture was stirred for 30min at 40°C, warmed to room temperature and stirred for a further 15min. The reaction was then cooled to 0°C and anhydrous HCl (0.71ml, 1.0M, 0.71mmol) in ether added. The mixture was left to stir at this temperature for 15min and then allowed to warm to RT. The solvent was removed *in vacuo* and the residue taken up in dry Et_2O. The solution was passed through a pad of dry celite, dried ($MgSO_4$) and the solvent removed *in vacuo*. The residue was purified by flash chromatography (petrol/DCM, 3/1) to give silylthiophene pinacolato-boronic ester **11** as a pale yellow oil (371mg, 51%). R_f 0.40 (3:1, petrol/DCM); ^{1}H NMR ($CDCl_3$): δ 0.26 (s, 6H), 0.87 (t, J = 7, 3H), 0.90 (s, 9H), 1.27-1.32 (m, 18H), 1.57 (t, J = 8, 2H), 2.87 (t, J = 8, 2H), 7.12 (s, 1H); ^{13}C NMR ($CDCl_3$) δ -4.83 (2xq), 14.17 (q), 16.86 (s), 22.67 (t), 24.86 (4xq), 26.44 (3xq), 29.08 (t), 29.98 (t), 31.72 (t), 32.02 (t), 83. 44 (s), 138.38 (d), 144.89 (s), 155.32 (s), (absent: SCB); IR (neat) 2955, 2927, 2857, 1525, 1470, 1435, 1370, 1332, 1298, 1271, 1250, 1214, 1166, 1144, 1047, 1008 cm^{-1}; MS (ES+) *m/z* 409 (MH); HRMS (ES+) calcd. for $C_{22}H_{42}BO_2SSi$ (MH) 409.2768, found 409.2770.

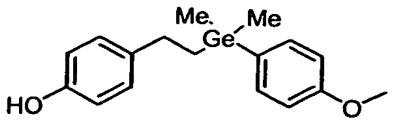
4-{2-[Dichloro-(4-methoxy-phenyl)-germanyl]-ethyl}-phenol 12



To magnesium (1.01g, 42mmol) in THF (25ml) was added 4-bromoanisole (5.21ml, 42mmol) and the mixture was heated briefly to initiate Grignard formation. After stirring for 1hr the grey solution was added drop-wise to a solution of germyl chloride (1.25g, 4.2mmol) in THF at RT. The yellow reaction mixture was then left stirring at this temperature for 16 hrs before quenching drop-wise with water until no effervescence occurs. The solvent was the removed *in vacuo* and the residue taken up in DCM (30ml). To the solution was added 1N HCl (5ml) with stirring and then conc. HCl (60ml). The resultant mixture was stirred vigorously for 40min before extracting the HCl layer with DCM (3x50ml), the combined organic extracts dried ($MgSO_4$) and the solvent removed *in vacuo*. The residue was taken up in DCM (50ml) and 0.5M NaOH (aq) (100ml) and the aqueous layer extracted with DCM (3x50ml). To the aqueous layer was then added 1N HCl (15ml) with shaking and then conc. HCl (100ml). The aqueous layer was then extracted with DCM (3x100ml), the combined organic extracts dried ($MgSO_4$) and the solvent removed *in vacuo* to give **12** as an orange/brown oil (1.25g, 84%). ^{1}H NMR ($CDCl_3$): δ 1.96-2.02 (m, 2H), 2.83-2.90 (m, 2H), 3.75 (s, 3H), 4.84 (s, 1H), 6.65 (d, J = 8.5, 2H), 6.88 (d, J = 9, 2H), 6.99 (d, J = 8.5, 2H), 7.40 (d, J = 9, 2H); ^{13}C NMR ($CDCl_3$) δ 27.81 (t), 28.55 (t), 55.39 (q), 114.58 (2xd), 115.51 (2xd), 126.72 (s), 129.35 (2xd), 133.76 (2xd, s), 154.07 (s), 162.12 (s); IR (neat) 3019, 2931, 2839, 2361, 1591, 1514, 1442,

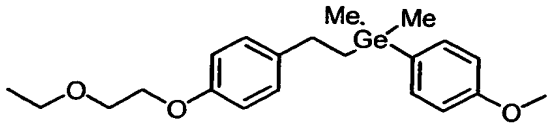
1403, 1290, 1254 cm^{-1}; MS (EI+) *m/z* 372 (M^+); HRMS calcd. for $C_{15}H_{16}Cl_2Ge^{74}O_2$ (M) 371.9739, found 371.9749.

4-{2-[(4-Methoxy-phenyl)-dimethyl-germanyl]-ethyl}-phenol 13



A solution of MeMgBr (1.01mL, 3.0M, 3.03mmol) in Et_2O was added to a solution of dichlorogermane **12** (184mg, 0.49mmol) in THF (3mL). The mixture was then refluxed at 110°C for 16h before partitioning between sat. NH_4Cl (aq) (100mL) and Et_2O (100mL). After extracting further with Et_2O (2x100mL) the combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo*. Purification by flash chromatography (petrol/EtOAc, 3/1) gave dimethylgermane **13** as a pale yellow oil (125mg, 74%). R_f 0.4 (petrol/EtOAc, 3/1); ^1H NMR ($CDCl_3$): δ 0.25 (s, 6H); 1.11-1.18 (m, 2H), 2.51-2.57 (m, 2H), 3.73 (s, 3H), 4.67 (s, 1H), 6.64 (d, J = 8.5, 2H), 6.84 (d, J = 9, 2H), 6.95 (d, J = 8.5, 2H), 7.29 (d, J = 9, 2H); ^{13}C NMR ($CDCl_3$) δ -3.56 (2xq), 18.21 (t), 30.22 (t), 55.13 (q), 113.84 (2xd), 115.14 (2xd), 128.94 (2xd), 132.15 (s), 134.48 (2xd), 137.01 (s), 153.45 (s), 159.85 (s); IR (neat) 3401 (broad), 3020, 2931, 2905, 2838, 1612, 1592, 1569, 1513, 1500, 1462, 1443, 1358, 1279, 1246, 1181, 1093 cm^{-1}; MS (EI+) *m/z* 332 (M^+); HRMS calcd. for $C_{17}H_{22}Ge^{74}O_2$ (M) 332.0832, found 332.0824.

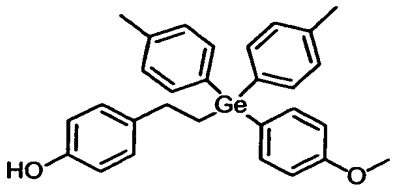
{2-[4-(2-Ethoxy-ethoxy)-phenyl]-ethyl}-(4-methoxy-phenyl)-dimethyl-germane 14



To a solution of dimethylgermane **13** (96.1mg, 0.29mmol) in acetonitrile (1ml) was added 2-chlorodiethyl ether (0.070mL, 0.64mmol), tetra-*n*-butylammonium iodide (10.7mg, 0.03mmol) and cesium carbonate (153mg, 0.44mmol). The mixture was refluxed at 85°C for 17h then cooled and filtered. The solvent was removed *in vacuo* and the residue purified by flash chromatography (petrol/EtOAc, 9/1) to give the title compound **14** as a pale yellow oil (106mg, 90%). R_f 0.3 (petrol/EtOAc, 9/1); ^1H NMR ($CDCl_3$): δ 0.25 (s, 6H); 1.12-1.19 (m, 5H), 2.52-2.56 (m, 2H), 3.52 (q, J = 7, 2H), 3.70 (t, J = 4.5, 2H), 3.73 (s, 3H), 4.01 (t, J = 4.5, 2H), 6.64 (d, J = 8.5, 2H), 6.84 (d, J = 10.5, 2H), 6.95 (d, J = 9, 2H), 7.29 (d, J = 9, 2H); ^{13}C NMR ($CDCl_3$) δ -3.53 (2xq), 15.23 (q), 18.19 (t), 30.24 (t), 55.06 (q), 66.86 (t), 67.53 (t), 69.08 (t), 113.81 (2xd), 114.55 (2xd), 128.71 (2xd), 132.03 (s), 134.47 (2xd), 137.06 (s), 156.93 (s), 159.94 (s); IR (neat) 2930, 2871, 1611, 1593, 1568,

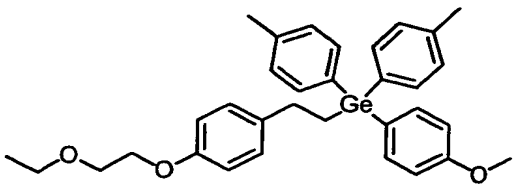
1511, 1500, 1458, 1280, 1247, 1181, 1125 cm^{-1}; MS (EI+) *m/z* 404 (M^+); HRMS calcd. for $C_{21}H_{30}Ge^{74}O_3$ (M) 404.1407, found 404.1393.

4-{2-[(4-Methoxy-phenyl)-di-*p*-tolyl-germanyl]-ethyl}-phenol 15



To oven dried Mg (120mg, 5.00mmol) in THF (3ml) was added 4-bromotoluene (855mg, 5.00mmol) drop-wise. Grignard formation was initiated by heating and after the magnesium had disappeared it was added to a solution of dichlorogermane **12** (186mg, 0.50mmol) in THF (3mL). The mixture was then refluxed at 110°C for 16h before partitioning between sat. NH_4Cl (aq) (100mL) and Et_2O (100mL). After extracting further with Et_2O (2x100mL) the combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo*. Purification by flash chromatography (petrol/EtOAc, 3/1) gave ditolylgermane **15** as a yellow oil (280mg, 92%). R_f 0.4 (petrol/EtOAc, 3/1); ^1H NMR ($CDCl_3$): δ 1.72-1.80 (m, 2H), 2.36 (s, 6H), 2.70-2.77 (m, 2H), 3.81 (s, 3H), 4.64 (s, 1H), 6.71 (d, J = 8.5, 2H), 6.92 (d, J = 8.5, 2H), 7.04 (d, J = 8.5, 2H), 7.19 (d, J = 8, 4H), 7.38 (d, J = 8, 4H), 7.40 (d, J = 8.5, 2H); ^{13}C NMR ($CDCl_3$) δ 16.63 (t), 21.58 (2xq), 30.43 (t), 55.19 (q), 114.17 (2xd), 115.31 (2xd), 128.18 (s), 129.03 (2xd), 129.19 (4xd), 133.79 (2xs), 135.02 (4xd), 136.33 (2xd), 137.14 (s), 138.77 (2xs), 153.62 (s), 160.31 (s); IR (neat) 3409 (broad), 3012, 2921, 2861, 1593, 1568, 1512, 1442, 1392, 1281, 1247, 1180, 1089, 1031 cm^{-1}; MS (EI+) *m/z* 484 (M^+); HRMS (EI+) calcd. for $C_{29}H_{30}Ge^{74}O_2$ (M^+) 484.1458, found 484.1446.

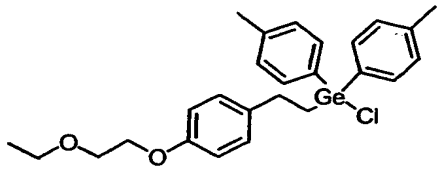
{2-[4-(2-Ethoxy-ethoxy)-phenyl]-ethyl}-(4-methoxy-phenyl)-di-*p*-tolyl-germane 16



To a solution of ditolylgermane **15** (9.57g, 20.0mmol) in acetonitrile (40ml) was added 2-chlorodiethyl ether (4.56mL, 41.5mmol), tetra-*n*-butylammonium iodide (739mg, 2.0mmol) and cesium carbonate (14.1g, 40.0mmol). The mixture was refluxed at 85°C for 17h then cooled and filtered. The solvent was removed *in vacuo* and the residue purified by flash chromatography (petrol/EtOAc, 9/1) to give the title compound **16** as a colourless oil (7.81g, 70%). R_f 0.5 (petrol/EtOAc, 9/1); ^1H NMR ($CDCl_3$): δ 1.24 (t, J = 7, 3H), 1.72-1.80

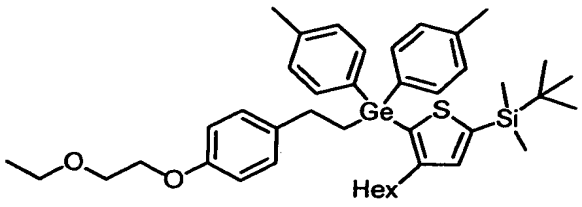
(m, 2H), 2.36 (s, 6H), 2.70-2.78 (m, 2H), 3.59 (q, J = 7, 2H), 3.77 (t, J = 5.5, 2H), 3.81 (s, 3H), 4.09 (q, J = 5.5, 2H), 6.82 (d, J = 8.5, 2H), 6.92 (d, J = 8.5, 2H), 7.07 (d, J = 8.5, 2H), 7.18 (d, J = 8, 4H), 7.38 (d, J = 8, 4H), 7.40 (d, J = 8.5, 2H); ^{13}C NMR ($CDCl_3$) δ 15.29 (q), 16.57 (t), 21.55 (2xq), 30.39 (t), 55.11 (q), 66.91 (t), 67.59 (t), 69.12 (t), 114.07 (2xd), 114.66 (2xd), 127.96 (s), 128.75 (2xd), 129.13 (4xd), 133.76 (2xs), 134.98 (4xd), 136.27 (2xd), 137.22 (s), 138.70 (2xs), 157.04 (s), 160.37 (s); IR (neat) 3010, 2972, 2925, 1593, 1567, 1510, 1454, 1392, 1281, 1247, 1180, 1090, 1031 cm^{-1}; MS (EI+) *m/z* 556 (M^+); HRMS (EI+) calcd. for $C_{33}H_{38}Ge^{74}O_3$ (M^+) 556.2033, found 556.2042.

Chloro-{2-[4-(2-ethoxy-ethoxy)-phenyl]-ethyl}-di-p-tolyl-germane 17



To anisolegermane **16** (100mg, 0.18mmol) was added HCl (7.0ml, 1.0M, 7.0mmol) in Et_2O and the reaction left to stir for 16hrs. The solvent was then removed *in vacuo* to give chlorogermane **17** as a colourless oil (85.3mg, 98%). ^{1}H NMR ($CDCl_3$): δ 1.24 (t, J = 7, 3H), 1.85-1.92 (m, 2H), 2.37 (s, 6H), 2.80-2.87 (m, 2H), 3.60 (q, J = 7, 2H), 3.77 (t, J = 5, 2H), 4.08 (q, J = 5, 2H), 6.81 (d, J = 8.5, 2H), 7.07 (d, J = 8.5, 2H), 7.23 (d, J = 8, 4H), 7.45 (d, J = 8, 4H); ^{13}C NMR ($CDCl_3$) δ 15.29 (q), 21.63 (t), 21.59 (2xq), 29.20 (t), 66.90 (t), 67.60 (t), 69.08 (t), 114.74 (2xd), 128.89 (2xd), 129.41 (4xd), 132.32 (2xs), 133.49 (4xd), 135.57 (s), 140.36 (2xs), 157.26 (s); IR (neat) 2973, 2924, 2868, 1610, 1584, 1511, 1453, 1393, 1300, 1247, 1177, 1125, 1090 cm^{-1}; MS (EI+) *m/z* 483 (M^+); HRMS (EI+) calcd. for $C_{26}H_{31}ClGe^{74}O_2$ (M^+) 484.1224, found 484.1207; Anal. calcd. for $C_{26}H_{31}ClGe^{74}O_2$: C 64.58, H 6.46, Cl 7.33, found C 64.12, H 6.56, Cl 7.68.

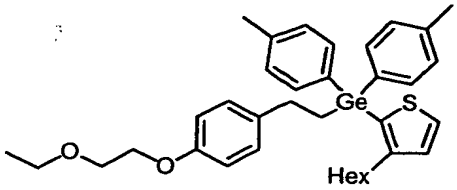
***tert*-Butyl-[5-({2-[4-(2-ethoxy-ethoxy)-phenyl]-ethyl}-di-*p*-tolyl-germanyl)-4-hexyl-thiophen-2-yl]-dimethyl-silane 18**



A solution of LDA (4.71mL, 2.0M, 1.13mmol) in hexanes/THF/ethylbenzene was added drop-wise to a degassed solution of silylthiophene **10** (1.18g, 6.28mmol) in THF (20mL) at -50°C. This solution was warmed to -40°C, stirred for 40min at this temperature and

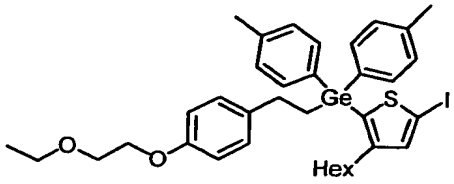
recooled to -50°C. It was then transferred by cannula to a degassed solution of chloroditolylgermane **17** (2.69g, 5.56mmol) in THF (20mL) at -50°C. The resulting mixture was stirred for 1hr at -40°C, warmed to RT and stirred for a further 1hr. After quenching with sat. NH_4Cl (aq) (50mL), the mixture was extracted with Et_2O (3x50mL), the combined organic extracts dried ($MgSO_4$) and the solvent removed *in vacuo*. Purification by flash chromatography (petrol/EtOAc, 9/1) gave silylthiopheneditolylgermane **18** as a pale yellow oil (803mg, 80%). R_f 0.3 (9/1, petrol/EtOAc); ^1H NMR ($CDCl_3$): δ 0.27 (s, 6H), 0.78 (t, J = 7.5, 3H), 0.80-1.26 (m, 21H), 1.76-1.84 (m, 2H), 2.35 (s, 6H), 3.36-3.42 (m, 2H), 2.69-2.73 (m, 2H), 3.59 (q, J = 7, 2H), 3.76 (t, J = 5, 2H), 4.08 (q, J = 5, 2H), 6.81 (d, J = 8.5, 2H), 7.05 (d, J = 8.5, 2H), 7.17 (d, J = 8, 4H), 7.18 (s, 1H), 7.39 (d, J = 8, 4H); ^{13}C NMR ($CDCl_3$) δ -4.60 (2xq), 14. 22 (q), 15.35 (q), 17.08 (s), 18.42 (t), 21.61 (2xq), 22.70 (t), 26.62 (3xq), 29.42 (t), 30.51 (t), 31.36 (t), 31.72 (t), 31.78 (t), 66.92 (t), 67.63 (t), 69.18 (t), 114.71 (2xd), 128.85 (2xd), 129.16 (4xd), 133.59 (2xs), 134.57 (s), 134.88 (4xd), 137.19 (s), 138.12 (d), 138.82 (2xs), 142.42 (s), 151.65 (s), 157.13 (s); IR (neat) 2955, 2929, 2857, 1610, 1509, 1457, 1391, 1300, 1278, 1250, 1177, 1122, 1087 cm^{-1}; MS (EI+) *m/z* 730 (M^+). HRMS (EI+) calcd. for $C_{42}H_{60}Ge^{74}O_2SSi$ (M^+) 730.3295, found 730.3298.

{2-[4-(2-Ethoxy-ethoxy)-phenyl]-ethyl}-(3-hexyl-thiophen-2-yl)-di-*p*-tolyl-germane 19



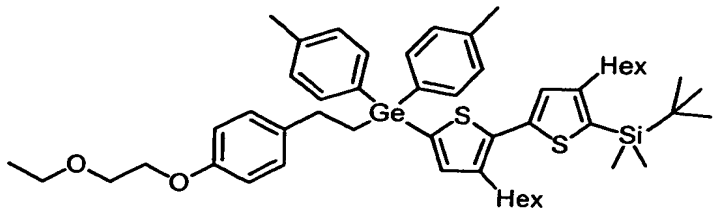
To silyl protected germylthiophene **18** (225mg, 0.31mmol) in DMF (3mL) was added ceasium fluoride (234mg, 1.54mmol) and the mixture left to stir for 24hrs at 110°C. The reaction mixture was partitioned between Et_2O (40mL) and water (75ml) and the Et_2O layer extracted with water (3x40ml). The organic layer was dried ($MgSO_4$), the solvent removed *in vacuo* and the residue purified by flash chromatography (petrol/EtOAc, 9/1) to give germylthiophene **19** as a pale yellow oil (182mg, 95%). R_f 0.3 (petrol/EtOAc, 9/1); ^1H NMR ($CDCl_3$): δ 0.81 (t, J = 7.5, 3H), 0.83-1.37 (m, 11H), 1.80-1.87 (m, 2H), 2.35 (s, 6H), 2.44 (t, J = 8, 3H), 2.74-2.82 (m, 2H), 3.61 (q, J = 7, 2H), 3.79 (t, J = 5, 2H), 4.10 (q, J = 5, 2H), 6.84 (d, J = 8.5, 2H), 7.09 (d, J = 8.5, 2H), 7.12 (d, J = 5, 1H), 7.20 (d, J = 8, 4H), 7.43 (d, J = 8, 4H), 7.54 (d, J = 5, 1H); ^{13}C NMR ($CDCl_3$) δ 14. 28 (q), 15.39 (q), 18.41 (t), 21.64 (2xq), 22.73 (t), 29.43 (t), 30.61 (t), 31.59 (t), 31.77 (t), 31.83 (t), 66.95 (t), 67.67 (t), 69.21 (t), 114.77 (2xd), 128.89 (2xd), 129.24 (4xd), 130.09 (d), 130.33 (d), 133.51 (2xs), 134.86 (4xd, s), 137.09 (s), 138.97 (2xs), 150.84 (s), 157.20 (s); IR (neat) 2929, 2860, 1610, 1510, 1457, 1392, 1300, 1258, 1245, 1178, 1123, 1087 cm^{-1}; MS (EI+) *m/z* 616 (M^+); HRMS (EI+) calcd. for $C_{36}H_{46}Ge^{74}O_2S$ (M^+) 616.2430, found 616.2435.

{2-[4-(2-Ethoxy-ethoxy)-phenyl]-ethyl}-(3-hexyl-5-iodo-thiophen-2-yl)-di-*p*-tolyl-germane 20



A solution of LDA (0.545mL, 2.0M, 1.09mmol) in hexanes/THF/ethylbenzene was added drop-wise to a solution of germylthiophene **19** (224mg, 0.36mmol) in THF (3mL) at -50°C. After stirring for 40min at -40°C, a solution of degassed 1,2-diiodoethane (1.56g, 5.52mmol) in THF (2mL) was added by cannula at -50°C. The resulting mixture was stirred in the dark for 1hr at –40°C, warmed to RT and stirred for a further 1hr. The reaction mixture was partitioned between sat. $Na_2S_2O_3$ (aq) (200mL) and Et_2O (100ml), extracted with Et_2O (2×100mL), the organics combined and then dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue purification by flash chromatography (petrol/EtOAc, 9/1) to give germylthiopheneiodide **20** as a pale yellow oil (251mg, 94%). R_f 0.5 (petrol/EtOAc, 9/1); ^1H NMR ($CDCl_3$): δ 0.79 (t, J = 7.5, 3H), 0.87-1.30 (m, 11H), 1.76-1.83 (m, 2H), 2.34-2.41 (m, 8H), 2.71-2.78 (m, 2H), 3.60 (q, J = 7, 2H), 3.78 (t, J = 5, 2H), 4.09 (q, J = 5, 2H), 6.82 (d, J = 8.5, 2H), 7.06 (d, J = 8.5, 2H), 7.17 (s, 1H), 7.19 (d, J = 8, 4H), 7.38 (d, J = 8, 4H); ^{13}C NMR ($CDCl_3$) δ 14. 16 (q), 15.29 (q), 18.15 (t), 21.57 (2xq), 22.58 (t), 29.22 (t), 30.40 (t), 31.31 (t), 31.52 (t), 31.65 (t), 66.89 (t), 67.59 (t), 69.11 (t), 77.71 (s), 114.70 (2xd), 128.75 (2xd), 129.24 (4xd), 132.83 (2xs), 134.66 (4xd, s), 136.72 (s), 139.15 (2xs), 139.75 (d), 152.70 (s), 157.13 (s); IR (neat) 2925, 2857, 1610, 1510, 1454, 1393, 1299, 1246, 1178, 1124, 1087 cm^{-1}; MS (ES+) *m/z* 765 (MNa); HRMS (ES+) calcd. for $C_{36}H_{45}Ge^{74}INaO_2S$ (MNa) 765.1295, found 765.1266.

***tert*-Butyl-[5'-({2-[4-(2-ethoxy-ethoxy)-phenyl]-ethyl}-di-*p*-tolyl-germanyl)-4,3'-dihexyl-[2,2']bithiophen-5-yl]-dimethyl-silane 21**



To a degassed solution of silylthiophene pinacolato-boronic ester **11** (256mg, 1.05mmol) and germylthiopheneiodide **20** (155mg, 0.21mmol) in DMF (1mL) was added $Pd(PPh_3)_4$ (23.1mg, 0.02mmol) and the resulting mixture stirred at 60°C for 24hr. The reaction

mixture was partitioned between water (100mL) and Et_2O (50ml), extracted with Et_2O (2×50mL) and the organics combined and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue purification by flash chromatography (petrol/DCM, 2/1) to give silyl protected germyldithiophene **21** as a yellow oil (112mg, 60%). R_f 0.5 (petrol/DCM, 2/1); ^1H NMR ($CDCl_3$): δ 0.27 (s, 6H), 0.75-1.36 (m, 34H), 1.76-1.84 (m, 2H), 2.32-2.39 (m, 8H), 2.71-2.80 (m, 4H), 3.59 (q, J = 7, 2H), 3.76 (t, J = 5, 2H), 4.08 (q, J = 5, 2H), 6.82 (d, J = 8.5, 2H), 6.99 (s, 1H), 7.07 (d, J = 8.5, 2H), 7.11 (s, 1H), 7.18 (d, J = 8, 4H), 7.42 (d, J = 8, 4H); ^{13}C NMR ($CDCl_3$) δ -4.96 (2xq), 14. 11 (2xq), 15.21 (q), 16.94 (s), 18.23 (t), 21.50 (2xq), 22.56 (t), 22.66 (t), 26.41 (3xq), 29.25 (t), 29.31 (2xt), 30.41 (t), 30.71 (t), 31.33 (t), 31.67 (2xt), 31.78 (t), 66.84 (t), 67.53 (t), 69.06 (t), 114.61 (2xd), 128.42 (d), 128.71 (2xd), 128.97 (s), 129.08 (4xd), 133.26 (2xs), 134.72 (4xd), 135.06 (s), 136.49 (s), 136.99 (s), 138.34 (d), 138.87 (2xs), 140.18 (s), 141.12 (s), 151.03 (s), 156.99 (s); IR (neat) 2924, 2854, 1610, 1509, 1455, 1390, 1246, 1175, 1124, 1086, 1007 cm^{-1}; MS (EI+) *m/z* 896 (M^+). HRMS (ES+) calcd. for $C_{52}H_{74}Ge^{74}NaO_2S_2Si$ (MNa^+) 919.4009, found 919.4001.

Example 2

To further exemplify the invention, example 2 relates to a solution phase model of a high purity arylamine oligomer using a germyl linker. Assembly of the oligomer is a stepwise process in which each monomer unit is added sequentially through repetitive transition metal mediated coupling in order to obtain highly pure and well-defined structures.
The model reactions for a solid phase synthesis is outlined in Figure 11 and whose steps may be summarised as

Step 1: attachment and functionalisation of the germyl linker
Step 2: attachment of the first TBDMS protected monomer
Step 3: cleavage of TBDMS protecting group
Step 4: conversion to a triflate coupling precursor
Step 5: cross-coupling of a second monomer
Step 6: removal of the oligomer from the germanium-based linker

Steps 3, 4 and 5 represent the repetitive steps for the oligomer build-up. The role of the TBDMS group is to protect the phenol during the Suzuki-type cross-coupling.

Step 1: (Figure 12)

Arylgermane **3** was prepared by transmetalation with lithiated (4-bromo-phenoxy)-*tert*-butyl-dimethyl-silane **22** in 77 % yield. TBDMS protecting group in *tert*-butyl-[4-({2-[4-(2-ethoxy-ethoxy)-phenyl]-ethyl}-dimethyl-germanyl)-phenoxy]-dimethyl-silane **28** was then cleaved using tetrabutylammonium fluoride in THF to give gave germylphenol **29** in 76 % yield, with no detectable cleavage of the germyl linker. Conversion of germylphenol

29 into germyltrifluoromethanesulfonate using trifluoromethanesulfonic anhydride in anhydrous pyridine **30** was achieved in 87 % yield.

Step 2: (Figure 13)

The first TBDMS protected amine monomer **34** was attached to germyltrifluoromethanesulfonate **33** was cross-coupled with monomer **34,** using a Suzuki-type protocol, with 5 % mol $Pd(PPh_3)_4$ in 1,2-dimethoxyethane at 80 °C, to to give germylamine **31** in 84% yield. No detectable cleavage of the germyllinker and of the TBDMS protecting group occurs under these conditions.

Step 3: (Figure 14)

Cleavage of the TBDMS protecting group in germylamine **31** was achieved using tetrabutylammonium fluoride in THF and gave germylphenol **32** in 90 % yield with no detectable cleavage of the germyl linker.

Step 4: (Figure 15)

Conversion of the germylphenol **32** into the germyltrifluoromethanesulfonate **33** was achieved using trifluoromethanesulfonic anhydride in anhydrous pyridine. Under these conditions, compound **33** was prepared in 86 % yield.

Step 5: (Figure 16)

Germyltrifluoromethanesulfonate **33** was coupled to the amine monomer **25** using 5% mol $Pd(PPh_3)_4$ in 1,2-dimethoxyethane at 80 °C to give germylamine **34** in 71 % yield. No detectable cleavage of the germyl linker occurs under these conditions.

Step 6: (Figure 17)

This step is carried out as described in ***step 5*** in example 1.

Figure 11 illustrates the envisaged key steps in the iterative solid phase synthesis of an arylamine.

Figure 12 illustrates the attachment and the functionnalisation of the germyl linker.

Figure 13 illustrates linking of a protected arylamine monomer to the germyl linker.

Figure 14 illustrates a proposed deprotection protocol.

Figure 15 illustrates a proposed conversion into a trifluoromethanesulfonate protocol.

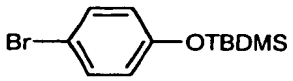
Figure 16 illustrates a proposed coupling protocol.

Figure 17 illustrates a proposed cleavage protocol.

Experimental procedures

All compounds were characterised by NMR spectroscopy, elemental analysis and/or mass spectrometry and found to be consistent with the expected structures.

(4-Bromo-phenoxy)-*tert*-butyl-dimethyl-silane 22

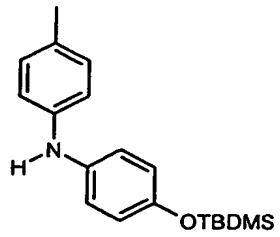


This compound was prepared in a similar way to that described in G. R. Pettit, M. P. Grealish, M. K.Jung, E. Hamel, R. K. Robin, J.-C. Chapuis, J. M. Schmidt, J. Med. Chem, *45*, 12, **2002**, 2534-2542.

tert-Butyldimethylsilylchloride (18.40 g, 12.2×10^{-2} mol) was added slowly to a solution of 4-bromophenol (19.99 g, 11.6×10^{-2} mol) and imidazole (16.2 g, 23.8×10^{-2} mol) in *N,N*-dimethylformamide (50 mL) at room temperature. The mixture was stirred at room temperature for 24 h. The mixture was then partitioned between water and hexane. The organic layer was separated off and the aqueous phase was further extracted with hexane. The combined organic fractions were dried over magnesium sulfate, filtered and concentrated *in vacuo* to give a colourless oil (32.89 g, 11.5×10^{-2} mol).

Yield: 99 %

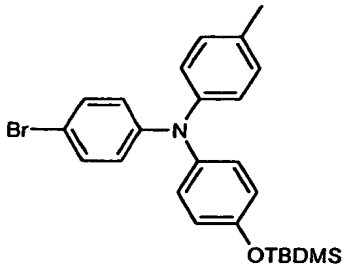
[4-(*tert*-Butyl-dimethyl-silanyloxy)-phenyl]-*p*-tolyl-amine 23



Procedure A

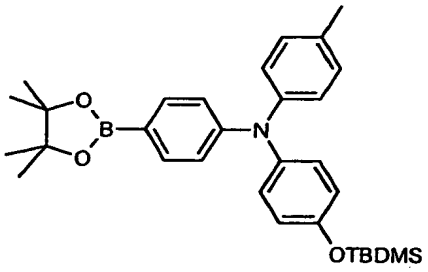
A solution of *p*-toluidine (6.41 g, 5.98×10^{-2} mol), (4-bromo-phenoxy)-*tert*-butyl-dimethyl-silane **22** (15.64 g, 5.44×10^{-2} mol), sodium *tert*-butoxide (6.73 g, 7.00×10^{-2} mol), *rac*-binap (0.23 g, 0.37×10^{-3} mol), $Pd_2(dba)_3$, (dba=dibenzylidene acetone), (0.48 g, 0.52×10^{-3} mol) in toluene (200 mL) was stirred vigorously overnight at 100 °C. The crude product was a brown oil. Purification by column chromatography (eluent: dichloromethane/hexane 1/3) gave the expected product as a colourless oil (12.6 g, 4.02×10^{-2} mol). Yield: 74 %.

(4-Bromo-phenyl)-[4-(*tert*-butyl-dimethyl-silanyloxy)-phenyl]-*p*-tolyl-amine 24



This compound was prepared according to procedure A from [4-(*tert*-butyl-dimethyl-silanyloxy)-phenyl]-*p*-tolyl-amine **23** (7.00 g, 1.80×10^{-2} mol), 4-bromo-iodo-benzene (5.53 g, 1.95×10^{-3} mol), sodium *tert*-butoxide (3.71 g, 3.86×10^{-2} mol), *rac*-binap (0.11 g, 0.17×10^{-3} mol) and $Pd_2(dba)_3$ (0.05 g, 0.06×10^{-3} mol) in toluene (150 mL). The reaction mixture was then cooled to room temperature and filtered. The filtrate was taken up in diethylether, washed with water, dried over magnesium sulfate, filtered and concentrated *in vacuo* to give a brown oil. Purification by column chromatography (eluent: dichloromethane/hexane 1/5) gave the expected product as a colourless solid (5.4 g, 1.15×10^{-2} mol). Yield: 52 %.

[4-(*tert*-Butyl-dimethyl-silanyloxy)-phenyl]-[4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-*p*-tolyl-amine 25

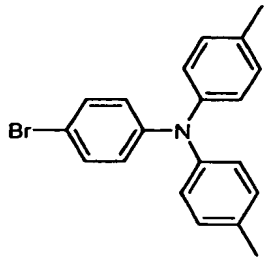


Procedure B

A solution of *n*-butyllithium (2.5M in hexane) (2.61 mL, 6.53×10^{-3} mol) was added drop-wise to a solution of (4-bromo-phenyl)-[4-(*tert*-butyl-dimethyl-silanyloxy)-phenyl]-*p*-tolyl-amine **24** (2.04 g, 4.35×10^{-3} mol) in tetrahydrofuran cooled at - 78 °C. The resulting mixture was stirred at - 78 °C for 1 h. 2-Isopropoxy-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (1.21 g, 6.50×10^{-3} mol) was added to the resulting solution and after 15 minutes, the reaction mixture was allowed to warm up to room temperature and stirred overnight. The mixture was then partitioned between water and dichloromethane. The organic layer was separated off and the aqueous phase was extracted with dichloromethane. The combined organic fractions were dried over magnesium sulfate, filtered and concentrated *in vacuo* to give a yellow solid.

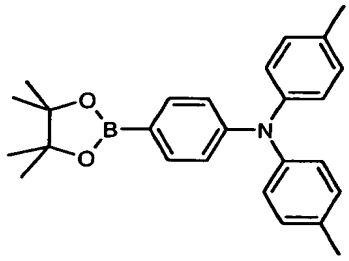
Recrystallisation from MeOH afforded the expected product as white needles (1.58 g, 3.06×10^{-3} mol). Yield: 70 %.

(4-Bromo-phenyl)-di-*p*-tolyl-amine 26



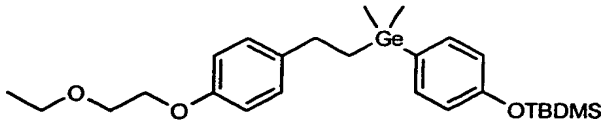
Di-*p*-tolyl-amine (25.00 g, 12.7×10^{-2} mol), 4-bromo-iodobenzene (43 g, 15.2×10^{-2} mol), potassium hydroxyde (79.6 g, 141.9×10^{-2} mol) were suspended in *o*-xylene (100 mL) and the mixture was then heated to 100 °C. To this suspension were added copper chloride (2.51 g, 2.5×10^{-2} mol) and 1,10-phenanthroline (4.57 g, 2.5×10^{-2} mol) and the mixture was stirred vigorously 1 h at 145 °C. Toluene was then added and the reaction mixture was filtered. The filtrate was concentrated *in vacuo* to give a brown oil. Purification by column chromatography (eluent : hexane) and recrystallisation from methanol gave the expected product as a white solid (24.4 g, 6.92×10^{-2} mol). Yield: 55 %.

[4-(4,4,5,5-Tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-di-*p*-tolyl-amine 27



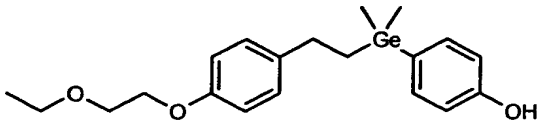
This compound was prepared according to procedure B from (4-bromo-phenyl)-di-*p*-tolyl-amine **26** (2.00 g, 5.68×10^{-3} mol), *n*-butyllithium (2.5M in hexane) (3.4 mL, 8.50×10^{-3} mol) and 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (1.58 g, 8.50×10^{-3} mol). The combined organic fractions were dried over magnesium sulfate, filtered and concentrated *in vacuo* to give a light yellow solid. Recrystallisation from MeOH afforded the expected product as white needles (1.60 g, 4.00×10^{-3} mol). Yield: 71 %.

tert-Butyl-[4-({2-[4-(2-ethoxy-ethoxy)-phenyl]-ethyl}-dimethyl-germanyl)-phenoxy]-dimethyl-silane 28



A solution of *n*-butyllithium (2.5 M in hexane) (5.8 mL, 1.45×10^{-2} mol) was added drop-wise to a solution of (4-bromo-phenoxy)-*tert*-butyl-dimethyl-silane **22** (4.16 g, 1.45×10^{-2} mol) in tetrahydrofuran (40 mL) at -78 °C. After being stirred for 45 min, the mixture was transferred by cannula to a solution of {2-[4-(2-ethoxy-ethoxy)-phenyl]-ethyl}-dimethyl-germyl-chloride (2.25 g, 6.79×10^{-3} mol) in toluene (50 mL) at -78 °C. The mixture was stirred for 3 h at room temperature. The reaction was then quenched with an aqueous solution of HCl (1 M) and extracted with diethylether. The organic fractions were collected, dried over magnesium sulfate, filtered and concentrated *in vacuo* to give a yellow oil. Purification by column chromatography (eluent : hexane/ethyl acetate 10/1) gave the expected product as a colourless liquid (2.63 g, 5.23×10^{-3} mol).
Yield: 77 %

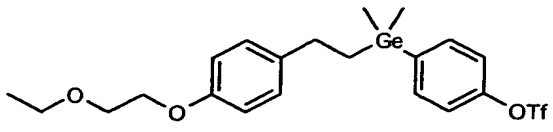
4-({2-[4-(2-Ethoxy-ethoxy)-phenyl]-ethyl}-dimethyl-germanyl)-phenol 29



Procedure C

A solution of tetrabutylammonium fluoride (1.54 g, 4.88×10^{-3} mol) in tetrahydrofuran (50 mL) was added drop-wise to a solution of *tert*-butyl-[4-({2-[4-(2-ethoxy-ethoxy)-phenyl]-ethyl}-dimethyl-germanyl)-phenoxy]-dimethyl-silane **28** (2.45 g, 4.88×10^{-3} mol) in tetrahydrofuran (100 mL) at room temperature. The resulting mixture was stirred at room temperature for 30 min. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane and washed with water. The organic layer was then dried over magnesium sulfate, filtered and concentrated *in vacuo* to give a yellow oil. Purification by column chromatography (eluent : hexane/ethyl acetate 4/1) gave the expected product as a colourless liquid (1.42 g, 3.70×10^{-3} mol). Yield: 76 %.

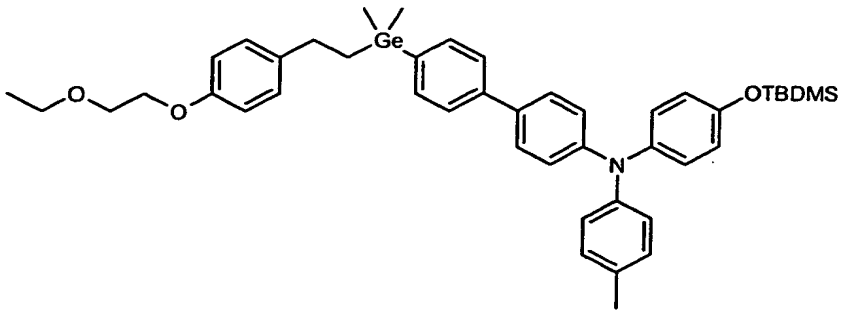
4-({2-[4-(2-Ethoxy-ethoxy)-phenyl]-ethyl}-dimethyl-germanyl)-phenyl-trifluoromethanesulfonate 30



Procedure D

Trifluoromethanesulfonic anhydride (0.88 g, 3.12×10^{-3} mol) was added slowly to a solution of 4-({2-[4-(2-ethoxy-ethoxy)-phenyl]-ethyl}-dimethyl-germanyl)-phenol **29** (1.22 g, 3.14×10^{-3} mol) in pyridine (6 mL) at 0 °C. The resulting mixture was stirred at 0 °C for 5 min, then allowed to warm to room temperature and stirred at this temperature for a further 16 h. The reaction mixture was then poured into water and extracted with diethylether. The organic fractions were collected, washed sequentially with water, 10 % aqueous HCl solution, water and brine, dried over magnesium sulfate, filtered and concentrated *in vacuo* to give a yellow oil. Purification by column chromatography (eluent : hexane/ethyl acetate 5/1) gave the expected product as a colourless liquid (1.42 g, 2.72×10^{-3} mol). Yield: 87 %.

[4-(*tert*-Butyl-dimethyl-silanyloxy)-phenyl]-[4'-({2-[4-(2-ethoxy-ethoxy)phenyl]-ethyl}-dimethyl-germanyl)-biphenyl-4-yl]-*p*-tolyl-amine 31

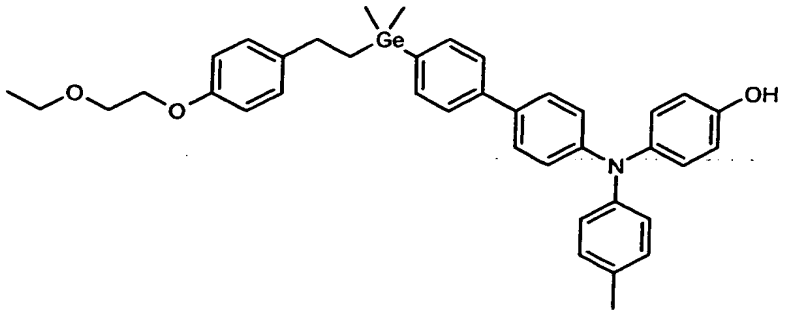


Procedure E

A mixture of 4-({2-[4-(2-ethoxy-ethoxy)-phenyl]-ethyl}-dimethyl-germanyl)-phenyl-trifluoromethanesulfonate **30** (0.40 g, 0.77×10^{-3} mol), [4-(*tert*-butyl-dimethyl-silanyloxy)-phenyl]-[4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-*p*-tolyl-amine **25** (0.40 g, 0.77×10^{-3} mol), $Pd(PPh_3)_4$ (44 mg, 3.8×10^{-5} mol), aqueous Na_2CO_3 (2M) (8 mL) in 1,2-dimethoxyethane (8 mL) was heated at 80 °C with vigorous stirring. After 2 h, the reaction was cooled to room temperature and the solvent was removed under reduced pressure. The residue was then partitioned between dichloromethane and 2M Na_2CO_3 aqueous solution. The organic phase was separated and the aqueous phase was extracted further

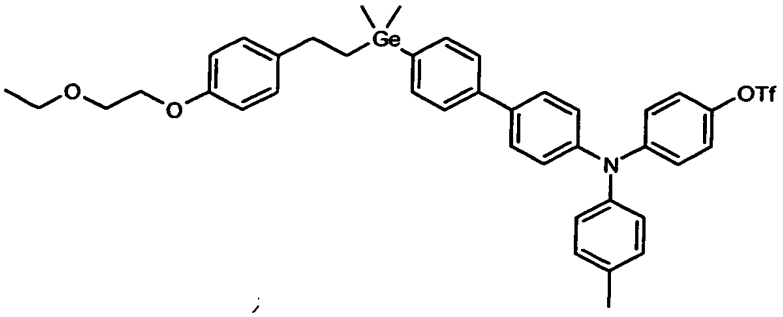
with dichloromethane. The dichloromethane fractions were combined and dried over magnesium sulfate, filtered and concentrated *in vacuo* to give a brown oil. Purification by column chromatography (eluent : hexane/ethyl acetate 19/1) gave the expected product as a colourless oil (0.49 g, 0.64×10^{-3} mol). Yield: 84 %.

4-{[4'-({2-[4-(2-Ethoxy-ethoxy)-phenyl]-ethyl}-dimethyl-germanyl)-biphenyl-4-yl]-*p*-tolyl-amino}-phenol 32



This compound was prepared according to procedure C from [4-(*tert*-butyl-dimethyl-silanyloxy)-phenyl]-[4'-({2-[4-(2-ethoxy-ethoxy)phenyl]-ethyl}-dimethyl-germanyl)-biphenyl-4-yl]-*p*-tolyl-amine **31** (0.46 g, 0.60×10^{-3} mol) and tetrabutylammonium fluoride (0.20 g, 0.63×10^{-3} mol) in tetrahydrofuran (23 mL) After removal of the solvent under reduced pressure, the residue was dissolved in dichloromethane and the organic solution was washed with water. The organic phase was then separated, dried over magnesium sulfate, filtered and concentrated *in vacuo* to give a yellow oil. Purification by column chromatography (eluent : hexane/ethyl acetate 7/3) gave the expected product as a colourless oil (0.35 g, 0.54×10^{-3} mol). Yield: 90 %.

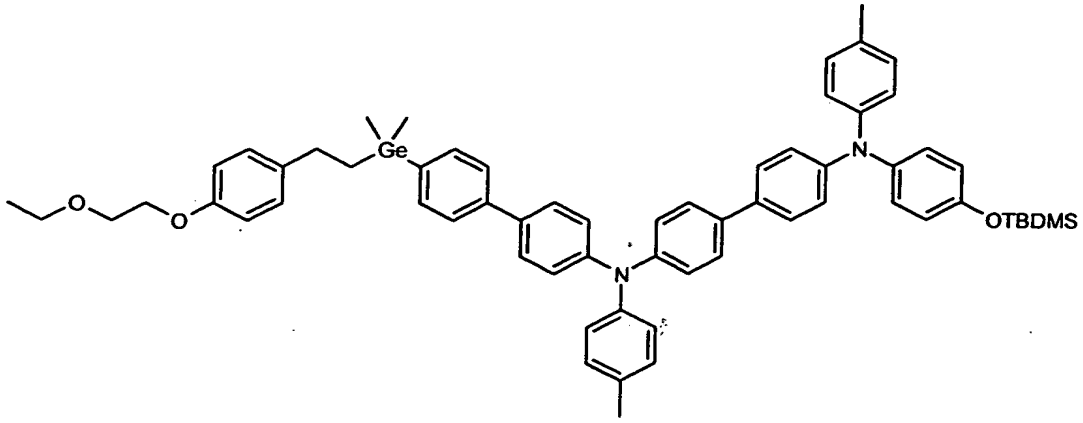
4-{[4'-({2-[4-(2-Ethoxy-ethoxy)-phenyl]-ethyl}-dimethyl-germanyl)-biphenyl-4-yl]-*p*-tolyl-amino}-phenyl-trifluoromethanesulfonate 33



This compound was prepared according to procedure D from 4-{[4'-({2-[4-(2-ethoxy-ethoxy)-phenyl]-ethyl}-dimethyl-germanyl)-biphenyl-4-yl]-*p*-tolyl-amino}-phenol **32** (0.33 g,

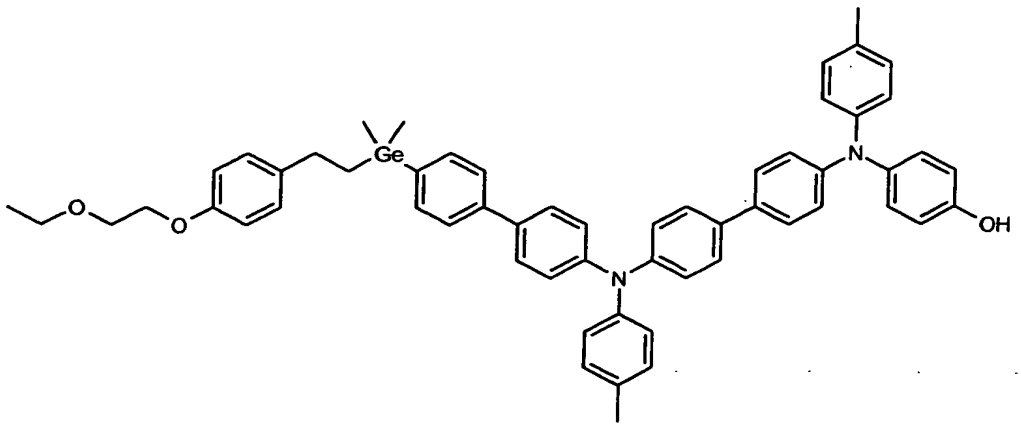
$0.50x10^{-3}$ mol) and trifluoromethanesulfonic anhydride (0.14 g, $0.50x10^{-3}$ mol) in pyridine (5 mL). The reaction mixture was poured into water and extracted with Et_2O. The organic fractions were collected, washed sequentially with water, 10 % aqueous HCl solution, water and brine. The organic solution was dried over magnesium sulfate, filtered and concentrated *in vacuo* to give a yellow oil. Purification by column chromatography (eluent : hexane/ethyl acetate 10/1) gave the expected product as a colourless glassy solid (0.34 g, $0.44x10^{-3}$ mol). Yield: 86 %.

$N^{4'}$-[4-(tert-Butyl-dimethyl-silanyloxy)-phenyl]-N^4-[4'-({2-[4-(2-ethoxy-ethoxy)-phenyl]-ethyl}-dimethyl-germanyl)-biphenyl-4-yl]-N^4,$N^{4'}$-di-*p*-tolyl-biphenyl-4,4'-diamine 34



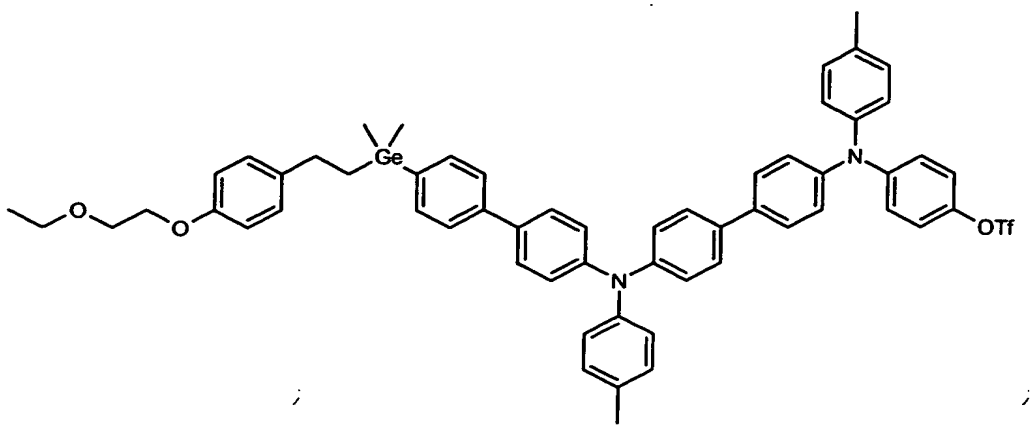
This compound was prepared according to procedure E from 4-{[4'-({2-[4-(2-ethoxy-ethoxy)-phenyl]-ethyl}-dimethyl-germanyl)-biphenyl-4-yl]-*p*-tolyl-amino}-phenyl-trifluoromethanesulfonate **33** (0.30 g, $0.39x10^{-3}$ mol), [4-(*tert*-butyl-dimethyl-silanyloxy)-phenyl]-[4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-*p*-tolyl-amine **25** (0.20 g, $0.39x10^{-3}$ mol), $Pd(PPh_3)_4$ (22 mg, $1.90x10^{-5}$ mol) and aqueous Na_2CO_3 (2M) (4 mL) in 1,2-dimethoxyethane (8 mL). After removal of the solvent under reduced pressure, the residue was partitioned between dichloromethane and 2 M Na_2CO_3 aqueous solution. The organic phase was separated and the aqueous phase was extracted with further portions of dichloromethane. The combined organic fractions were dried over magnesium sulfate, filtered and concentrated *in vacuo* to give a brown oil. Purification by column chromatography (eluent : hexane/ethyl acetate 20/1) gave the expected product as a colourless oil (0.28 g, $0.28x10^{-3}$ mol). Yield: 71 %.

4-[(4'-{[4'-({2-[4-(2-Ethoxy-ethoxy)-phenyl]-ethyl}-dimethyl-germanyl)-biphenyl-4-yl]-p-tolyl-amino}-biphenyl-4-yl)-*p*-tolyl-amino]-phenol 35



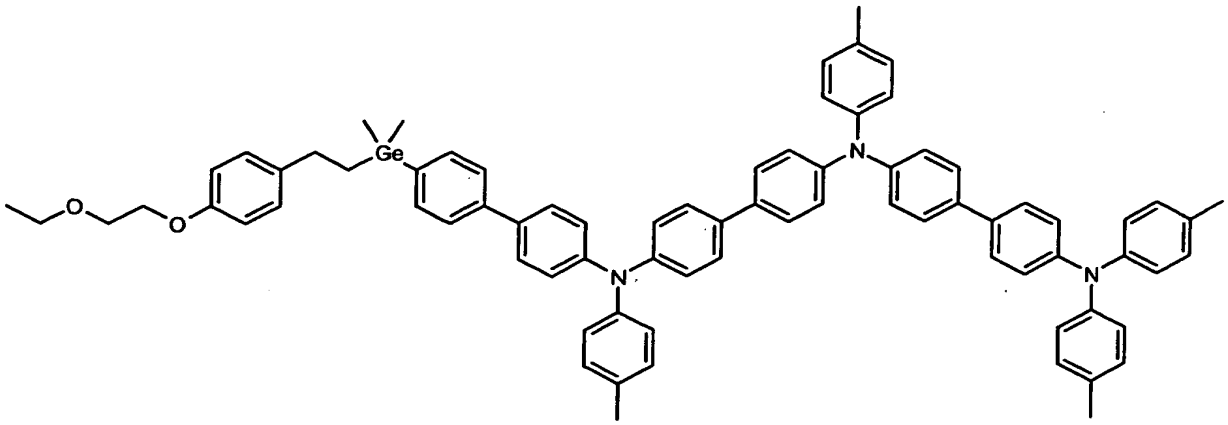
This compound was prepared according to procedure C from the $N^{4'}$-[4-(tert-butyl-dimethyl-silanyloxy)-phenyl]-N^{4}-[4'-({2-[4-(2-ethoxy-ethoxy)-phenyl]-ethyl}-dimethyl-germanyl)-biphenyl-4-yl]-N^{4},$N^{4'}$-di-*p*-tolyl-biphenyl-4,4'-diamine **34** (0.27 g, 0.26×10^{-3} mol) and tetrabutylammonium fluoride (0.09 g, 0.28×10^{-3} mol) in tetrahydrofuran (7 mL). After removal of the solvent under reduced pressure, the residue was dissolved in dichloromethane and washed with water. The organic phase was then dried over magnesium sulfate, filtered and concentrated *in vacuo* to give a yellow oil. Purification by column chromatography (eluent : hexane/ethyl acetate 3/1) gave the expected product as a colourless glassy solid (0.18 g, 0.20×10^{-3} mol). Yield: 75 %.

4-[(4'-{[4'-({2-[4-(2-Ethoxy-ethoxy)-phenyl]-ethyl}-dimethyl-germanyl)-biphenyl-4-yl]-p-tolyl-amino}-biphenyl-4-yl)-*p*-tolyl-amino]-phenyl-trifluoromethanesulfonate 36



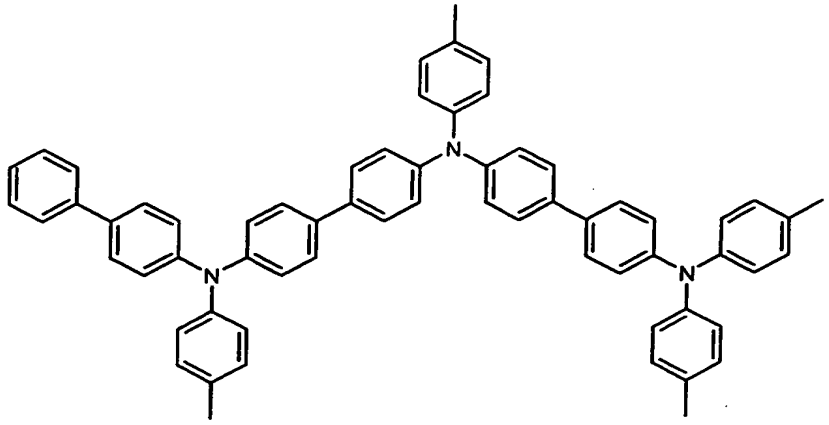
This compound was prepared according to procedure D from 4-[(4'-{[4'-({2-[4-(2-ethoxy-ethoxy)-phenyl]-ethyl}-dimethyl-germanyl)-biphenyl-4-yl]-p-tolyl-amino}-biphenyl-4-yl)-*p*-tolyl-amino]-phenol **35** (0.18 g, 0.20×10^{-3} mol) and trifluoromethanesulfonic anhydride (0.06 g, 0.20×10^{-3} mol) in pyridine (5 mL). The reaction mixture was poured into water and extracted with diethylether. The organic fractions were collected, washed sequentially with water, 10 % aqueous HCl solution, water and brine. The organic solution was dried over magnesium sulfate, filtered and concentrated *in vacuo* to give a yellow oil. Purification by column chromatography (eluent : hexane/ethyl acetate 10/1) gave the expected product as a colourless glassy solid (0.19 g, 0.18×10^{-3} mol). Yield: 92 %.

$N^{4'}$-[4'-(Di-*p*-tolylamino-biphenyl-4-yl]-N^4-[4'-({2-[4-(2-ethoxy-ethoxy)-phenyl]-ethyl}-dimethyl-germanyl)-biphenyl-4-yl]-N^4,$N^{4'}$-di-*p*-tolyl-biphenyl-4,4'-diamine 37



This compound was prepared according to procedure E from 4-[(4'-{[4'-({2-[4-(2-ethoxy-ethoxy)-phenyl]-ethyl}-dimethyl-germanyl)-biphenyl-4-yl]-p-tolyl-amino}-biphenyl-4-yl)-*p*-tolyl-amino]-phenyl-trifluoromethanesulfonate **36** (0.16 g, 0.15×10^{-3} mol), [4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-di-*p*-tolyl-amine **27** (0.06 g, 0.15×10^{-3} mol), $Pd(PPh_3)_4$ (9 mg, 0.78×10^{-5} mol) and aqueous Na_2CO_3 (2M) (2 mL) in 1,2-dimethoxyethane (5 mL). After removal of the solvent under reduced pressure, the residue was partitioned between dichloromethane and 2 M Na_2CO_3 aqueous solution. The organic phase was separated and the aqueous phase was extracted with further portions of dichloromethane. The combined organic fractions were dried over magnesium sulfate, filtered and concentrated *in vacuo* to give a brown oil. Purification by column chromatography (eluent : hexane/ethyl acetate 17/1) gave the expected product as a white solid (0.13 g, 0.11×10^{-3} mol). Yield: 75 %.

$N^{4'}$-[4'-(Di-*p*-tolylamino-biphenyl-4-yl]-N^4-(4'-biphenyl)-N^4,$N^{4'}$-di-*p*-tolyl-biphenyl-4,4'-diamine 38



A solution of $N^{4'}$-[4'-(Di-*p*-tolylamino-biphenyl-4-yl]-N^4-[4'-({2-[4-(2-ethoxy-ethoxy)-phenyl]-ethyl}-dimethyl-germanyl)-biphenyl-4-yl]-N^4,$N^{4'}$-di-*p*-tolyl-biphenyl-4,4'-diamine **37** (0.13 g, 0.11×10^{-3} mol) in trifluoroacetic acid (1 % in dichloromethane) (5 mL) was stirred at room temperature for 16 h. The solvent was then removed *in vacuo*, and the crude material was purified by column chromatography (eluent : hexane/ethyl acetate 10/1) to give the expected product as a white solid (0.08 g, 0.07×10^{-3} mol). Yield: 72 %.

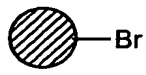
Example 3

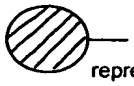
To further exemplify the invention, example 3 relates to assembly of a bithiophene unit in a stepwise process in which each monomer unit is added sequentially to the solid support.

Experimental

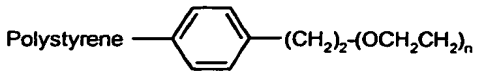
All compounds were characterised by gel phase NMR spectroscopy and by elemental analysis and were found to be consistent with the expected structures. Hypogel 200-OH is a low Mw cross-linked polystyrene resin and was purchased from Fluka chemicals.

Bromination of "Hypogel 200-OH" 39





represents Hypogel 200 resin:

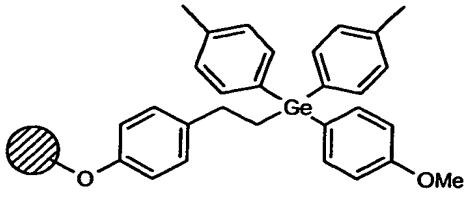


in this and all subsequent structures.

Carbon tetrabromide (26g, 78.4mmol) was added to a suspension of Hypogel 200-OH (24.55g, 19.6mmol) in dichloromethane (250 ml). This mixture was cooled to 0°C, and triphenylphosphine (10.30g, 39.3mmol) was added. The mixture was stirred at room temperature under nitrogen for 24h. After removal of the solvent by filtration, the resin was

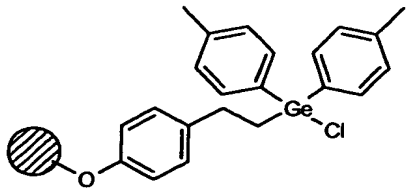
washed extensively with *N,N*-dimethylformamide (1x300mL), tetrahydrofuran/water (1:1) (2x300mL), tetrahydrofuran (2x300ml), methanol (2x300mL) and was dried for 16h at 50°C *under vacuo* to give **39** as pale yellow granules (25g). Loading level : 0.8 mmol.g^{-1} (estimated from Br analysis). Elemental analysis: C, 76.1; H, 7.9; Br 6.5 %)

Immobilisation of linker 40



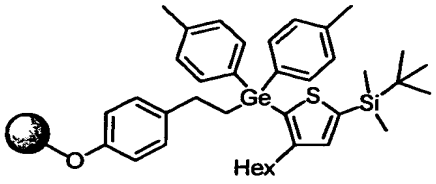
4-{2-[(4-Methoxy-phenyl)-di-p-tolyl-germanyl]-ethyl}-phenol (4.12g, 8.51mmol), tetra-*n*-butylammonium iodide (0.485g, 1.31mmol) and cesium carbonate (4.28g, 13.1mmol) was added to a suspension of resin **39** (5.45g, 4.38 mmol) in acetonitrile (30 ml). This mixture was stirred at 85°C for 22h. After removal of the solvent by filtration, the resin was washed extensively with acetonitrile (3x100mL), *N,N*-dimethylformamide (2x100mL), tetrahydrofuran/water (1:1) (3x100mL), tetrahydrofuran (2x100ml), methanol (2x100mL) and was dried for 16h at 50°C *under vacuo* to give **40** as pale yellow granules (7.71g). Loading level : 0.5 mmol.g^{-1} (estimated from Ge). Elemental analysis: C, 78.0; H, 7.7; Ge,3.5; Br, <1.5 %)

Electrophilic *Ipso*-Cleavage arylgermane 41



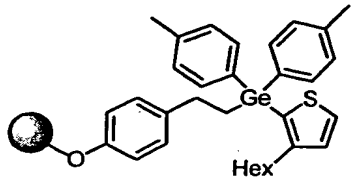
A solution of 1.0M HCl in diethylether (35mL, 35mmol) was added to resin **40** (7.30g, 6.3mmol). This mixture was stirred at room temperature under nitrogen for 20h. After removal of the solvent by filtration, the resin was washed with anhydrous diethylether (2x50mL) and dried at 50°C *under vacuo* for 16h to give resin **41** as pale yellow granules (6.4g). Loading level: 0.5 mmol.g^{-1} (estimated from Ge and Cl loadings. Elemental analysis: C, 76.7; H, 7.9; Ge, 3.6; Cl 2.2 %.

Immobilization of thiophene monomer 10 to give resin 42



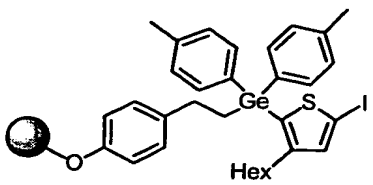
A solution of LDA (3.26mL, 2.0M, 6.5mmol) in hexanes/THF/ethylbenzene was added drop-wise to a degassed solution of silylthiophene **10** (1.80g, 6.4mmol) in THF (10mL) at -50°C. This solution was warmed to -40°C, stirred for 40min at this temperature and recooled to -50°C. It was then transferred by cannula to a degassed suspension of germylchloride resin **41** (3.35g, LL = 0.6mmolg^{-1}, 2.1mmol) in THF (10mL) at -50°C. The resulting mixture was stirred for 1hr at -40°C, warmed to RT and stirred for a further 16hr. After quenching with sat. NH_4Cl (aq) (100mL), the solvent was removed by filtration and the resin washed with DMF (100mLx3), THF:H_2O 1:1 (100mLx3), THF (100mLx3) and MeOH (100mLx3). The resin was then dried *in vacuo* at 60°C to give the required resin **42** as yellow grains (2.67g). Elemental analysis: C, 83.3; H, 7.7; N, 0.2; S, 0.4; Ge, 1.9%.

Deprotection of silyl protected thiophene to give resin 43



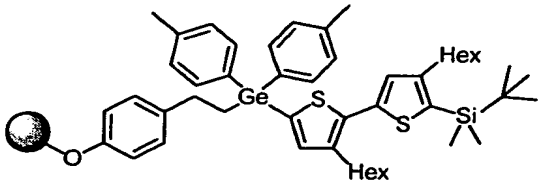
To silyl protected germylthiophene resin **42** (2.00g, LL = 0.6mmolg^{-1}, 1.24mmol) in DMF (5mL) was added ceasium fluoride (1.32g, 8.68mmol) and the mixture left to stir for 72hrs at 110°C. The solvent was then removed by filtration and the resin washed with DMF (75mLx2), THF:H_2O 1:1 (75mLx3), THF (75mLx3) and MeOH (75mLx3). The resin was then dried *in vacuo* at 60°C to give the required resin **43** as beige grains (1.58g). Elemental analysis: C, 84.0; H, 7.9; N, 0.2; S, 0.5; Ge, 1.8%.

Iodination of resin bound thiophene to give resin 44



A solution of LDA (1.10mL, 2.0M, 2.19mmol) in hexanes/THF/ethylbenzene was added drop-wise to a suspension of germylthiophene resin **43** (1.18g, LL = 0.6mmolg^{-1}, 0.73mmol) in THF (10mL) at -50°C. After stirring for 40min at -40°C, a solution of degassed 1,2-diiodoethane (1.03g, 3.65mmol) in THF (10mL) was added by cannula at -50°C. The resulting mixture was stirred in the dark for 1hr at –40°C, warmed to RT and stirred for a further 1hr. The solvent was then removed by filtration and the resin washed with $Na_2S_2O_3$ (aq) (75mLx3), THF:H_2O 1:1 (75mLx3), THF (75mLx3) and MeOH (75mLx3). The resin was then dried *in vacuo* at 60°C to give the required resin **44** as beige grains (0.98g). IR (neat) 3024, 2919, 1600, 1509, 1492, 1451, 1244, 1106, 1028 cm^{-1}. Elemental analysis: C, 83.0; H, 7.7; N, 0.3; S, 0.4; Ge, 1.7%.

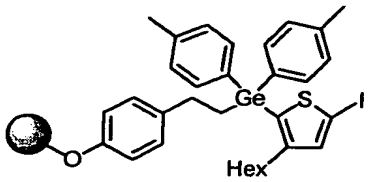
Suzuki cross-coupling on resin 44 to give resin 45



To a degassed solution of silylthiophene pinacolato-boronic ester **11** (502mg, 1.23mmol) and germylthiopheneiodide resin **44** (655mg, LL = 0.6, 0.41mmol) in DMF (5mL) was added $Pd(PPh_3)_4$ (23.1mg, 0.02mmol) and the resulting mixture stirred at 60°C for 24hr. The solvent was then removed by filtration and the resin washed with DMF (50mLx2), THF:H_2O 1:1 (50mLx3), THF (50mLx3) and MeOH (50mLx3). The resin was then dried *in vacuo* at 60°C to give the required resin **45** as beige grains (595mg). IR (neat) 3024, 2919, 1600, 1509, 1492, 1451, 1244, 1104, 1028 cm^{-1}. Elemental analysis: C, 82.6; H, 7.4; N, 0.2; S, 0.8%.

The following steps were carried out to demonstrate the "double coupling" on the resin

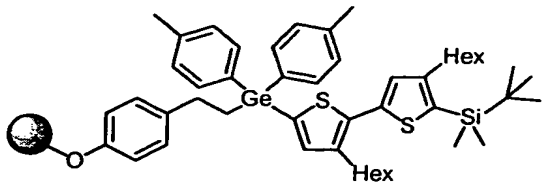
Iodination of resin bound thiophene 46



A solution of LDA (1.10mL, 2.0M, 2.19mmol) in hexanes/THF/ethylbenzene was added drop-wise to a suspension of germylthiophene resin **45** (314mg, LL = 0.6mmolg^{-1}, 0.19mmol) in THF (2mL) at -50°C. After stirring for 40min at -40°C, a solution of degassed 1,2-diiodoethane (267mg, 0.95mmol) in THF (1mL) was added by cannula at -50°C. The

resulting mixture was stirred in the dark for 1hr at –40°C, warmed to RT and stirred for a further 1hr. The solvent was then removed by filtration and the resin washed with $Na_2S_2O_3$ (aq) (50mLx3), THF:H_2O 1:1 (50mLx3), THF (50mLx3) and MeOH (50mLx3). The resin was then dried *in vacuo* at 60°C to give the required resin **46** as beige grains (272mg).

Suzuki cross-coupling on resin bound thiophene 47



To a degassed solution of silylthiophene pinacolato-boronic ester **11** (208mg, 0.51mmol) and germylthiopheneiodide resin **46** (272mg, LL = 0.6, 0.17mmol) in DMF (2mL) was added $Pd(PPh_3)_4$ (9.8mg, 0.008mmol) and the resulting mixture stirred at 60°C for 24hr. The solvent was then removed by filtration and the resin washed with DMF (50mLx2), THF:H_2O 1:1 (50mLx3), THF (50mLx3) and MeOH (50mLx3). The resin was then dried *in vacuo* at 60°C to give the required resin **47** as beige grains (262mg). Elemental analysis: C, 81.8; H, 7.0; N, 0.2; S, 0.8%.

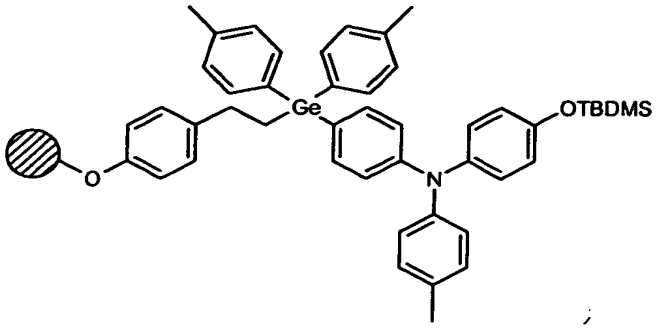
Example 4

To further exemplify the invention, example 4 relates to assembly of a triarylamine trimer unit in a stepwise process in which each monomer unit is added sequentially to the solid support.

Experimental

All compounds were characterised by gel phase NMR spectroscopy and by elemental analysis and were found to be consistent with the expected structures.

Attachment of arylamine monomer 24 to give resin 48

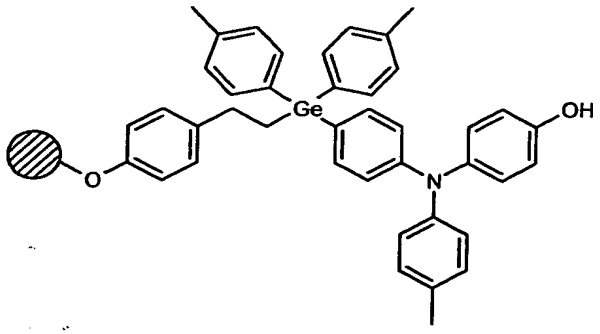


A solution of *n*-butyllithium (2.5 M in hexane) (3.4 mL, $5.4x10^{-3}$ mol) was added drop-wise to a solution of (4-Bromo-phenyl)-[4-(*tert*-butyl-dimethyl-silanyloxy)-phenyl]-*p*-tolyl-amine

24 (2.53 g, $5.4x10^{-3}$ mol) in tetrahydrofuran (20 mL) at -78 °C. After being stirred for 45 min, the mixture was transferred by cannula to a suspension of resin C (3.00 g, $1.5x10^{-3}$ mol) in toluene (30 mL) at -78 °C. The resulting mixture was stirred for 18 h at room temperature. An aqueous solution of HCl (1 M) was then added and the mixture stirred another 30min. After removal of the solvent by filtration, the resin was washed extensively with *N,N*-dimethylformamide (1x75mL), tetrahydrofuran/water (1:1) (2x75mL), tetrahydrofuran (2x75ml), methanol (2x75mL) and was dried for 18h at 50°C *under vacuo* to give resin **48** as pale yellow granules (3.23 g).

Elemental analysis: C, 80.2%; H, 8.0 %; N, 0.5 %; Ge, 2.7 %; Cl, <0.5 %

Deprotection of silyl protected resin 48 to give resin 49

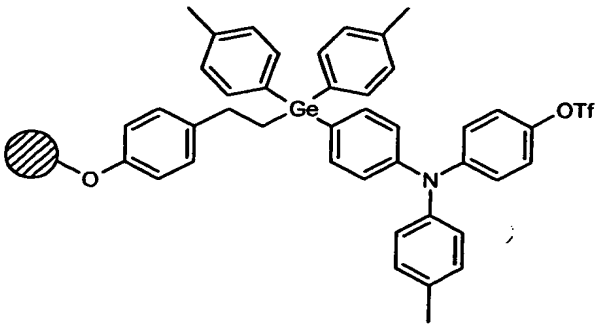


Procedure F

Tetrabutylammonium fluoride (1.34 g, $4.25x10^{-3}$ mol) was added to a suspension of resin **48** (2.43 g, $1.22x10^{-3}$ mol) in tetrahydrofuran (20 ml). This mixture was stirred under nitrogen at room temperature for 20h. After removal of the solvent by filtration, the resin was washed extensively with *N,N*-dimethylformamide (1x75mL), tetrahydrofuran/water (1:1) (2x75mL), tetrahydrofuran (2x75ml), methanol (2x75mL) and was dried for 16h at 50°C *under vacuo* to give resin **49** as pale yellow granules (2.33 g).

Elemental analysis: C, 80.8%; H, 7.7 %; N, 0.7 %; Ge, 2.8 %

Triflation of resin bound arylamine 49 to give resin 50

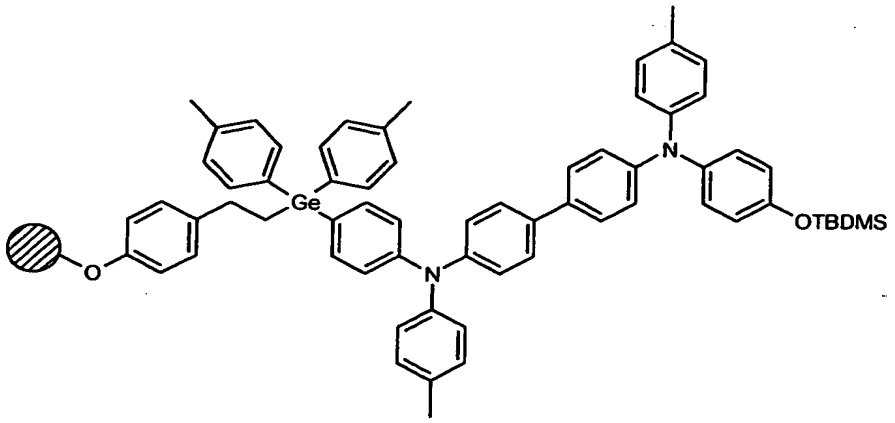


Procedure G

Trifluoromethanesulfonic anhydride (0.50 mL, $2.97x10^{-3}$ mol) was added slowly to a suspension of resin **49** (1.61 g, $0.81x10^{-3}$ mol) swollen in pyridine (10 mL) at 0 °C. The resulting mixture was stirred at 0 °C for 5 min, then allowed to warm to room temperature and stirred at this temperature for a further 16 h. After removal of the solvent by filtration, the resin was washed extensively with *N,N*-dimethylformamide (1x75mL), tetrahydrofuran/water (1:1) (2x75mL), tetrahydrofuran (2x75ml), methanol (2x75mL) and was dried for 16h at 50°C *under vacuo* to give resin **50** as pale yellow granules (1.73 g).

Elemental analysis: C, 76.3%; H, 6.7 %; N, 0.7 %; S, 1.3 %; F, 2.2 %; Ge, 2.7 %; N, 0.7 %;

Suzuki cross-coupling on resin 50 to give resin 51

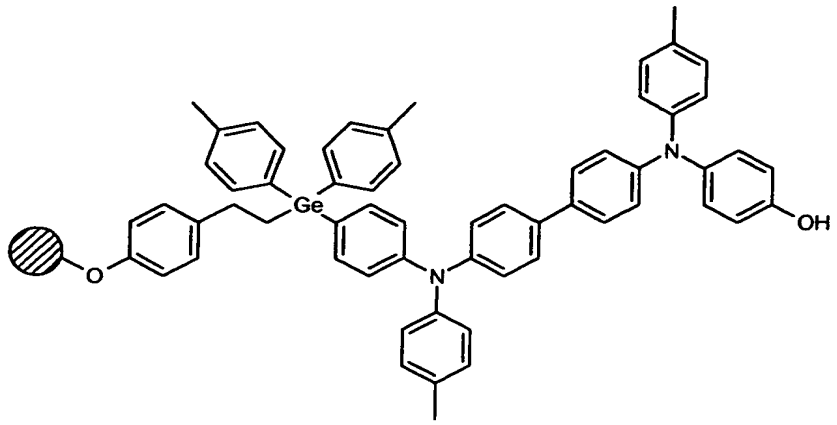


Procedure H

Resin **50** (1.34 g, $0.67x10^{-3}$ mol), [4-(*tert*-butyl-dimethyl-silanyloxy)-phenyl]-[4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-*p*-tolyl-amine **25** (1.73 g, $3.35x10^{-3}$ mol), $Pd(PPh_3)_4$ (0.15 g, $0.13x10^{-3}$ mol), aqueous Na_2CO_3 (2M) (10 mL) in 1,2-dimethoxyethane (10 mL) were stirred at 80 °C for 18h. After removal of the solvent by filtration, the resin was washed extensively with *N,N*-dimethylformamide (1x50mL), tetrahydrofuran/water (1:1) (2x50mL), tetrahydrofuran (2x50ml), methanol (2x50mL) and was dried for 16h at 50°C *under vacuo* to give resin **51** as dark brown granules (1.25 g).

Elemental analysis: C, 77.1 %; H, 7.0 %; N, 1.0 %; F, 2.2 %; Ge, 2.5 %

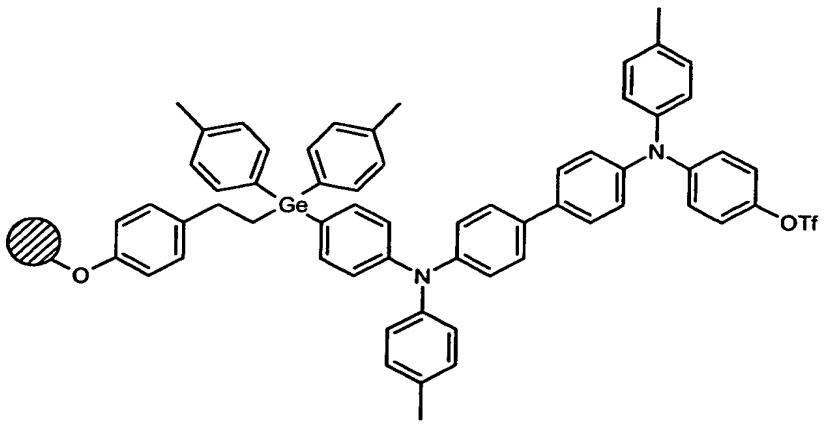
Deprotection of silyl protected resin 51 to give resin 52



This compound was prepared according to procedure F. Resin **51** (0.94 g, 0.47×10^{-3} mol) and tetrabutylammonium fluoride (0.74 g, 2.35×10^{-3} mol) were added together with tetrahydrofuran (10 mL). After removal of the solvent by filtration, the resin was washed extensively with *N,N*-dimethylformamide (1x30mL), tetrahydrofuran/water (1:1) (2x30mL), tetrahydrofuran (2x30ml), methanol (2x30mL) and was dried for 16h at 50°C *under vacuo* to give resin **52** as dark brown granules (0.91 g).

Elemental analysis: C, 78.5 %; H, 7.0 %; N, 1.0 %; Ge, 2.4%

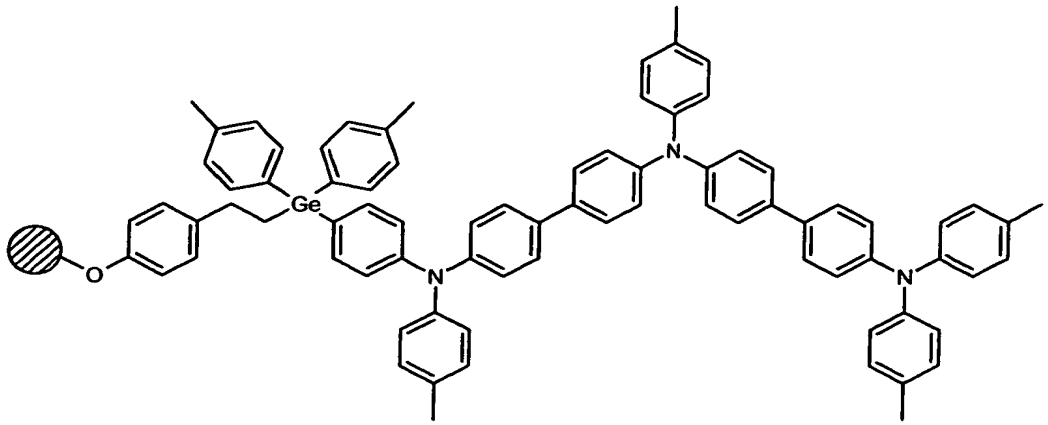
Triflation of resin bound arylamine 52 to give resin 53



This compound was prepared according to procedure G. Resin **52** (0.70 g, 0.35×10^{-3} mol) and trifluoromethanesulfonic anhydride (0.30 mL, 1.75×10^{-3} mol) were added together in tetrahydrofuran (10 mL). After removal of the solvent by filtration, the resin was washed extensively with *N,N*-dimethylformamide (1x30mL), tetrahydrofuran/water (1:1) (2x30mL), tetrahydrofuran (2x30ml), methanol (2x30mL) and was dried for 16h at 50°C *under vacuo* to give resin **53** as brown granules (0.65 g).

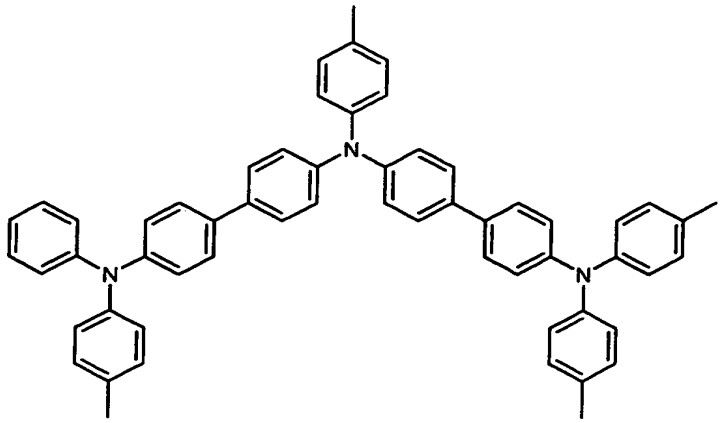
Elemental analysis: C, 67.9 %; H, 6.3 %; N, 1.1 %; S, 1.1 %; Ge, 2.2%

Suzuki cross-coupling on resin 53 to give resin 54



This compound was prepared according to procedure H. Resin **53** (0.53 g, 0.35×10^{-3} mol) was reacted in 1,2-dimethoxyethane (5 mL) with **27** (1.73 g, 3.35×10^{-3} mol), $Pd(PPh_3)_4$ (0.15 g, 0.13×10^{-3} mol) and aqueous Na_2CO_3 (2M) (5 mL). After removal of the solvent by filtration, the resin was washed extensively with *N,N*-dimethylformamide (1x30mL), tetrahydrofuran/water (1:1) (2x30mL), tetrahydrofuran (2x30ml), methanol (2x30mL) and was dried for 16h at 50°C *under vacuo* to give resin **54** as brown granules (0.47 g).
Elemental analysis: C, 72.0%; H, 6.2%; N, 1.3%; Ge, 2.2%

Cleavage of resin 54 to give $N^{4'}$-[4'-(Di-p-tolylamino-biphenyl-4-yl]-N^4-(4'-phenyl)-N^4,$N^{4'}$-di-p-tolyl-biphenyl-4,4'-diamine 55.



A suspension of resin **54** (0.33 g) in trifluoroacetic acid (10 % in dichloromethane) (5 mL) was stirred at room temperature for 16 h. The resin was separated off by filtration and washed with dichloromethane. The organic washings were concentrated 50°C *under vacuo* to give a dark brown oil. Purification by column chromatography (eluent :

ethylacetate:hexane 1:20) gave the expected product which was confirmed by ^{1}H and ^{13}C nmr spectroscopy.